### THE

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### PHYSICAL REVIEW.

# ON THE LATENT HEAT OF FUSION AND THE SPECIFIC HEAT OF SALTS IN THE SOLID AND LIQUID STATE.

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Contribution No. 28 from the Research Laboratory of Physical Chemistry, Mass. Institute of Technology. 1

THE latent heat of fusion of only a very few inorganic salts has been determined, and of the data known a number were obtained at an early date when the measurements were necessarily comparatively crude. Of the salts melting above 300° Landolt & Börnstein's Tabellen contain only the following:

Salt.	Molecular Heat of Fusion.	Reference.
KNO <sub>3</sub>	4,900	Persons, Pogg. Ann., 70, 300, 1846.
NaNO <sub>3</sub>	5,500	" " 74, 525, 1847.
PbBr <sub>2</sub>	4,500	Ehrhardt, Wiedemann Ann., 24, 257, 1885.
PbCl <sub>2</sub>	5,800	" " 24, 257, 1885.
$PbI_2$	5,300	" 24, 257, 1885.

It seemed to us, in the interest of obtaining additional information on the constitution of salts in the fused state, that further measurements of this important constant together with measurements of the specific heats of salts just above and below their melting point were desirable. The existing data on these specific heats are likewise scant and not in good agreement. In the present paper a convenient method for making these measurements with a fair degree

<sup>&</sup>lt;sup>1</sup> This research was carried out under a grant from the Wm. E. Hale Research Fund to the trustees, of which grateful acknowledgment of the aid furnished by them is hereby made.



of precision is described, and the results obtained with twelve different salts presented and discussed.

### METHOD AND APPARATUS.

General Method. - Briefly, the method adopted was to heat in an electric furnace, a known weight of the salt contained in a sealed platinum vessel, to a high temperature which was accurately measured. The vessel was then dropped into a calorimeter and the quantity of heat liberated determined. This experiment was repeated for a series of different initial temperatures extending over a range of 50 to 60 degrees, both below and above the melting point of the salt. By correcting for the heat capacity of the containing vessel, the quantity of heat Q required to raise one gram of the salt from room temperature to its initial temperature could be calculated. Plotting values of Q as ordinates and corresponding temperatures t as abscissæ, curves were obtained, the slope of which at any point gave the specific heat of the salt at the corresponding temperature, while the discontinuity in the value of Q at the melting point gave the latent heat of fusion for one gram of the salt.

The Containing Vessel. — The salt was contained in a hollow cylindrical vessel of platinum about 5 cm. high and 18 mm. in diameter. This was made from a sheet of platinum of proper dimensions which was shaped around a cylindrical brass model, and the joint soldered with gold in the oxy-hydrogen flame. One end of the hollow cylinder thus formed was closed by gold-soldering a thin sheet-platinum disc over it. The cylinder was then weighed, filled to about three fourths of its capacity with the purified dry salt, weighed again, and a similar platinum disc gold-soldered over the open end. The vessel and contents were again weighed in order to determine the total mass of platinum and gold. The salt was thus enclosed within a fluid-tight platinum vessel with which measurements could be repeated as many times as desired.

The Electric Furnace. — The platinum cylinder just described was heated in an electric furnace constructed as shown in vertical section, Fig. 1.

A is the platinum cylinder which fits nicely within a hollow

copper cylinder B. A is of such a diameter that when introduced at the top of the apparatus it slides down to its indicated position in contact with the copper cylinder surrounding it. The cylinder Ahas a small groove pressed into it to allow the insertion of the tip of a thermoelement T, between it and the copper cylinder.

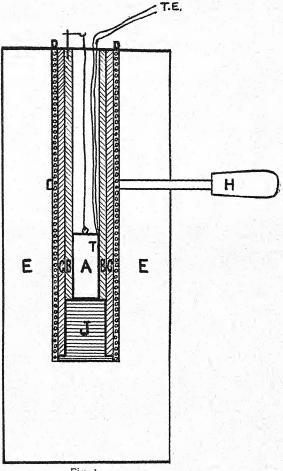


Fig. 1.

intimate contact assures uniformity of temperature between the platinum cylinder, the surrounding copper and the thermal junction. Surrounding the hollow copper cylinder is another similar one of iron, C, upon which a heating coil of asbestos-insulated nickelsteel wire D is wound. The iron cylinder extends about 10 cm. below the copper cylinder and is closed at the bottom during the heating by an iron piece J, which prevents the circulation of air currents within the heater.

The entire portion of the furnace thus far described was portable, and could be removed by means of the handle H from the heavy asbestos insulation E, into which it was set. The lead wires from the heating coil D were made long enough so that the heater could be removed from the asbestos shield and transported several feet to a position directly above the calorimeter, without interrupting the heating current. Upon lifting the heater, the iron piece J dropped out by its own weight and remained in E. A fine platinum wire was attached to the top of the cylinder A, so that it remained in position during the transportation to the calorimeter. This wire was cut at the desired instant, and the cylinder allowed to drop into the calorimeter.

The Calorimeter. — A platinum calorimeter of about 750 c.c. capacity was used. This was placed within a highly polished copper vessel, with an insulating air space of about one and one half inches between each. Surrounding the copper vessel on all sides but the top, was a water jacket separated from the former vessel by a two-inch air space; the whole was heavily insulated by a felt covering. The platinum and corresponding copper and felt covers had three openings in them to admit the stirrer, the thermometer, and the heated cylinder of salt, respectively. This last opening was provided with a thin mica cylinder extending about six inches vertically upward, which served to direct the falling hot cylinder into the calorimeter.

Stirring was accomplished by means of a flat strip of platinum which was bent into the arc of a circle to fit the calorimeter, the flat surface lying in a horizontal plane. A small motor operating a suitable mechanism gave this stirrer a vertical reciprocating motion, which produced a very effective agitation of the calorimetric liquid. With salts melting below 400°, water was used in the calorimeter while with salts of higher melting point aniline was used. This has the advantage of a low heat of vaporization and its specific heat is accurately known.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> Griffiths, Proc. Phys. Soc., 13, 234, 1894. Bartoli, Rend. Lomb. (2), 28, 1032, 1895.

A standard calorimeter thermometer, calibrated against a standard bearing a certificate from the Bureau of Standards at Washington, and which could easily be read to 0°.01 was used for measuring the rise of temperature in the calorimeter.

Temperature Measuring Apparatus. — The initial temperature to which the salt was heated was measured by a platinum-rhodium thermoelement, which was calibrated in the usual way with naphthalene, benzophenone and sulphur. The electromotive force of this couple was balanced against a Weston element through a very sensitive D'Arsonval galvanometer. The Weston element was compared with the laboratory standard element from time to time, and always found the same. Extraneous thermoelectromotive forces were compensated by an adjustable electromotive force introduced in the galvanometer circuit. Twenty millimeters deflection of the galvanometer corresponded to 1° change of temperature, the couple giving 8 microvolts per degree centigrade. The apparatus was identical with that used by Goodwin and Mailey in their work on the Density, Electrical Conductivity and Viscosity of Fused Salts, and described by them in detail in Phys. Rev., 25, 469, 1907.

Procedure, Sources of Error, Etc. - After the containing cylinder had been made and filled with salt, as already described, it was placed within the heater as shown in Fig. 1. The current (usually between 5 and 10 amperes), was turned on and at the expiration of about one half hour the desired temperature was attained. The current was then gradually diminished until no further rise in temperature was observed. An equilibrium temperature was thus finally reached, which with practice could be regulated to within 2° of any desired temperature; the temperature remained practically constant for hours. The salt was always kept at a constant temperature for at least one half hour before observations were begun. This was found to be sufficient to insure uniformity of temperature throughout the platinum cylinder. If the temperature chosen was slightly above the melting point of the salt, the equilibrium was approached from a somewhat higher temperature, to insure that all the salt was in the liquid state. During the ten minutes preceding the experiment proper, temperature (galvanometer) readings were made at one minute intervals, from which the exact temperature at

the instant of introducing the salt into the calorimeter could be determined. During this same time the calorimeter was mechanically stirred and readings of the calorimeter thermometer were also made at half minute intervals, in order that the exact temperature of the liquid at the instant the cylinder was introduced could be known, and also, to enable the cooling correction to be calculated. At the end of the ten minutes, the heater was removed to a position directly over the opening in the calorimeter, and the suspension holding the cylinder cut. At the outset it was feared that this operation might introduce considerable error. It was found, however, that the entire operation could be performed in less than one quarter of a minute, during which time the galvanometer deflections showed that no appreciable change in the temperature of the substance had occurred. The mass of metal immediately surrounding the platinum cylinder was so great that no noticeable change in temperature could take place during so short an interval. second possible source of error arising at this stage of the experiment was the loss of heat by radiation and convection during the time the cylinder was falling from the heater into the calorimeter. This transfer was made within a mica shield, and since the total distance from the heater to the surface of the liquid was only about ten inches the time required was only about one quarter of a second. The possible magnitude of the error arising from this source and from the evaporation of the calorimeter liquid (to be discussed below) was studied by measuring the specific heat of a cylinder of pure platinum by the above procedure. The mean specific heat of platinum between o° and 327° obtained in this way was 0.0344 which is in good agreement with the mean value of previous observations for the same interval. Hence only a very slight error could have been introduced by the heat loss during the transfer, probably not more than a small fraction of a per cent.

An obvious advantage of the arrangement employed is that the heater is removed from the neighborhood of calorimeter during the heating. During the transfer of the cylinder there is not enough heat absorbed by direct radiation from the heater through the multiple insulation of the calorimeter or through the cover to be observed by the calorimeter thermometer. This was tested by direct experiment.

Another possible source of error is that due to evaporation of the calorimeter liquid during the time the hot cylinder is passing through its surface. This was also tested by direct experiment, as follows: The platinum calorimeter, covered and filled with liquid as in the experiment proper, was placed on one scale of a sensitive balance. To this were added the cylinder, with its contained salt and suspending wire, these however, being placed without the calorimeter. The whole was carefully tared by weights placed on the other pan. Then the cylinder, supported by the fine suspending wire, was heated in a flame to approximately the highest temperature attained in the actual measurements, dropped into the calorimeter liquid, and any change of weight due to evaporation was noted. With aniline as a calorimeter liquid no change in weight was observed; with water when the cylinder was not heated above 450° the loss was less than 0.01 gram. This corresponds to a loss of less than five small calories which is negligible in comparison to the total heat effect of over 1,000 calories. Of course an appreciable quantity of water may have vaporized and recondensed upon the calorimeter cover, in which case there would be no attendant loss of weight or of heat.

The stirring was so efficient that the maximum temperature of the calorimeter and contents was reached in from three to seven minutes after the introduction of the hot substance. The total rise in temperature was from 2° to 4° and the cooling correction never more than a few hundredths of a degree. This correction was determined by the usual Rumford method. By adjusting the temperature of the water jacket of the calorimeter to a temperature approximately midway between the initial temperature of the calorimeter liquid and its final equilibrium temperature after the introduction of the salt, the correction was rendered very small. After each measurement the platinum cylinder was weighed to insure that no liquid had leaked into it. If the weight were found constant the cylinder and contents could be used again and again for as many determinations as desired. At least two different cylinders were used for the series of measurements on each salt and the results always found to be in good agreement. On the completion of a series of measurements with a given salt one end of the cylinder

was removed and the cylinder emptied and refilled with a new salt.

The heat capacity of the metal cylinder itself was determined by direct experiment by the method described above. The value obtained agreed with that calculated from previously obtained data on the specific heats of platinum and gold to within I per cent., its magnitude being less than one tenth the heat capacity of the salt. Hence if it were uncertain by one or two per cent. it would affect the final result by only that many tenths of a per cent.

Preparation of the Salts. — The salts used were those of the greatest chemical purity purchasable from Eimer and Amend. The soluble salts were further purified by repeated crystallization. The insoluble salts, such as the silver halides, were prepared by precipitation from silver nitrate which had been several times purified by recrystallization.

The sharpness of the transition point of the curves (see below) indicates that the salts were very free from impurities.

Scope of the Measurements. — The salts investigated were principally those whose electrical conductivity, viscosity and density had been previously determined, together with such additional nitrates and halides as it seemed might serve to bring to light any stoichiometrical relations existing between them. NaClO<sub>3</sub> was also studied in view of the recent interesting paper of Foot & Levy. The entire list of salts investigated is the following: KNO<sub>3</sub>, NaNO<sub>3</sub>, LiNO<sub>3</sub>, AgNO<sub>3</sub>, AgCl, TlCl, PbCl<sub>2</sub>, AgBr, TlBr, PbBr<sub>2</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and NaClO<sub>3</sub>.

#### RESULTS.

Experimental Data. — In Table I. are given all the experimental data. Q represents the total quantity of heat expressed in small calories required to raise one gram of salt from 25° C. to  $t^{\circ}$  centigrade.

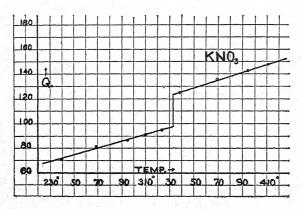
The above data are shown graphically in the following 12 plots, one for each of the salts studied. Plot 13 is an assemblage of all these curves drawn to the same scale on a single sheet. The ordinates represent the quantity of heat Q and the abscissæ the corresponding temperature t. The results of all determinations are given,

<sup>&</sup>lt;sup>1</sup>Lorenz & Kalmus, Zeit. Phys. Chem., 59, 17 and 244, 1907. Goodwin & Mailey, Phys. Rev., 25, 469 and 26, 1908. Goodwin & Kalmus, Phys. Rev., 27, 322, 1908. 
<sup>2</sup> Am. Chem. Jour., 37, 494.

TABLE I.

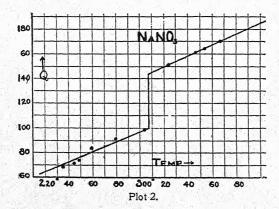
Salt.	Temp.	Q	Salt.	Temp.	Q	Salt.	Temp.	Q
KNO <sub>3</sub>	240°	70.2	TlBr	398°	17.5	AgCl	493°	68.9
**	268	80.3	46	427.5	18.8	"	511	70.0
**	295	86.5	66	453	19.7	**	533	72.7
"	310	90.5	"	487	35.4	K,Cr,O	329°	64.2
66	323	94.8	"	503.5	36.5	K <sub>2</sub> Cr <sub>2</sub> O	338	65.3
"	338	123.8	. "	504	36.5		375	74.2
"	369	135.8	"	521	38.0	46	376	74.5
"	394	142.0	AgNO <sub>3</sub>	168°	23.0	• • •	393	78.5
"	411	148.0	rigito 3	168	23.0		415.5	115.0
NaNO.	235°	68.4		179	26.0		475	134.5
114103	244	71.0	66	187.5	27.0		484	137.5
	249	74.7	66	195	29.0			
"	259	1 .	66	201	30.8	NaClO <sub>3</sub>	184°	39.8
"	279	84.0	**	219.5	49.0	66	192	43.0
66	303	91.6		219.5	49.9	£6	234.5	55.8
	323.5	98.5	"	230	50.9		240	56.7
"	347	151.2	"	246	53.3		249	60.8
"	1	161.0	"				249.5	61.6
"	353.5	164.0	"	250	54.3	66	259	114.1
	367	170.0		250	54.1 57.6	66	272	116.8
LiNO <sub>3</sub>	169°	48.2	**	268		66	272	117.3
**	193.5	55.9		268	57.2	- 66	278	118.8
- "	208	61.6	PbCl <sub>2</sub>	265°	16.9	"	299	125.0
- "	224	67.7	"	307.5	19.4	"	299	125.2
"	248	79.6	"	387	25.4	PbBr <sub>2</sub>	299°	14.4
"	256	168.6	- 66	498	35.0	10012	321	14.7
46	283	179.8	"	508	54.8	"	379	19.2
"	302.5	185.0	"	514	54.9		438	22.0
TICI	350°	17.7	"	519	54.3	44	475	23.7
1101	365	18.6		551	58.8		503	35.8
	382	19.0	66	559	59.4		560	40.0
	415	20.9	46	559.5	59.9	"	563	40.3
66	416.5	21.4	"	578	63.2		587	43.6
44	456	40.1	AgCl	371°	34.0			1 44
"	477		11601	403.5	36.8	AgBr	316°	24.7
"	477	41.3	"	408	37.6		341	25.2
"	527	41.1	**	435	40.0		395.5	30.3
"	- 1	44.3	66	443	41.3	"	408	31.6
	530	44.1	"	469	64.5	"	435	45.8
TlBr	321°	13.3		485	67.7	"	447	46.8
"	345	13.5		491	67.7	"	481	49.1
"	376	15.5		771	07.7	66	563	55.9

with the exception of a very few which deviated by eight or ten times the mean deviation of the others, and which it was fair to assume contained some huge accidental error. The first (lower) portion of each curve represents the data for the salt in the solid state, the third (upper) part in the liquid state, and the intercept of these lines on

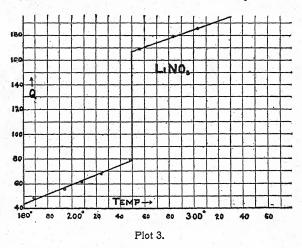


Plot 1.

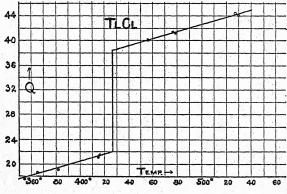
the ordinate through the melting point, gives the latent heat of fusion for one gram of the salt. The tangent of the angle which the first and third portions of the curve make with the axis of temperature gives the specific heat of the salt in the solid and liquid state respectively, in the neighborhood of the melting point. In drawing these



lines the best representative straight line has been chosen, i. e., no attempt has been made to take into account any variation in the specific heat with the temperature over a temperature interval of about 50° above and below the melting point. Further data will be necessary before this variation can be accurately determined.



It should be noticed that the data for the solid and liquid salt show no tendency to gradually merge into one another at the melting point as indicated by the dotted line on plot 7 for PbCl<sub>2</sub>.

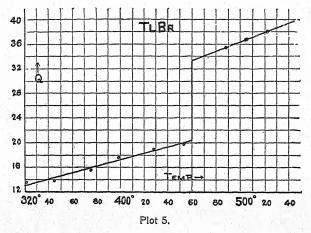


Plot 4.

This dotted line is the form of curve obtained by Ehrhardt,<sup>1</sup> for the lead halides, and is that which one would expect if the salt were impure.

From a discussion of our data we find that the combined effect <sup>1</sup> Wied. Ann., 24, 257, 1885.

of experimental errors and errors of plotting lead to results for the latent heat which are probably reliable to better than two per cent. It should be noted that owing to the slight difference in the slope of the lines locating data for the liquid and solid salt, an error of several degrees in the melting point introduces only a very slight error in the value of the latent heat as determined from the plot. The slope of the lines determining the specific heats, however, is probably not defined to this degree of precision, and the values of



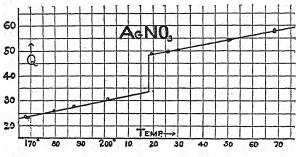
the specific heats in the two states may therefore be in error by as much as two per cent. or in some cases even more.

In the following Table II. are given the numerical values of the

TABLE II.

Salt.	M.P.	M	L	$\lambda = ML$	$\lambda/T$	C,	MC <sub>8</sub>	Cı
KNO <sub>3</sub>	308	101	25.5	2,570	4.5	0.292	29.5	0.333
NaNO <sub>3</sub>	333	85	45.3	3,690	6.1	0.388	33.0	0.430
LiNO <sub>8</sub>	250	69	88.5	6,100	11.5	0.387	26.7	0.390
AgNO <sub>a</sub>	218	170	15.2	2,580	5.3	0.195	33.2	0.195
AgCl	455	143	21.3	3,050	4.2	0.100	14.3	0.129
TICI	427	240	16.6	3,980	5.7	0.0580	13.9	0.0590
PbCl <sub>2</sub>	498	278	18.5	5,150	6.7	0.0778	21.6	0.121
AgBr	430	188	12.6	2,370	3.4	0.0755	14.2	0.0760
TlBr	460	284	12.7	3,610	5.0	0.0525	14.6	0.0800
PbBr <sub>2</sub>	488	367	9.9	3,650	4.9	0.0566	20.8	0.0780
NaClO <sub>8</sub>	255	106	49.6	5,250	10.0	0.320	32.4	0.325
K2Cr2O7	397	295	29.8	8,800	13.2	0.231	68.3	0.335

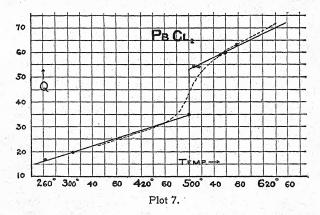
constants for the various salts, taken from plots drawn on accurately ruled paper, to such a scale that values could be interpolated to 0.1 cal. and 0.1°. From left to right the columns are: (MP) melting point of the salt, (M) molecular weight, (L) latent heat of fusion for



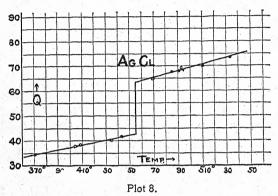
Plot 6.

I gm.,  $(\lambda = ML)$  molal heat fusion,  $(\lambda/T)$  ratio of molecular heat to the *absolute* melting point,  $(C_{\bullet})$  specific heat in the solid state,  $(MC_{\bullet})$  molecular heat of solid,  $(C_{\bullet})$  specific heat in the liquid state.

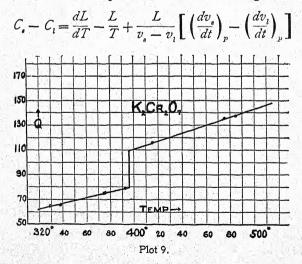
Heat of Fusion.—Stoichiometrical relations between the specific or the molecular heat of fusion and other properties of similar substances remain still to be discovered. The values of the molecular



heat of fusion show no apparent regularities, not even in the case of salts which crystallize in the same system and class. For instance, silver nitrate and potassium nitrate, both of which crystallize in rhombic prisms, have practically identical molal heats of fusion, while sodium nitrate and lithium nitrate which crystallize in the hexagonal system, calcite type, show no such equality, nor is it apparent with chlorides and bromides of the same type. Neither the latent heats of fusion of the salts themselves, nor the differences in them, show any simple functional relationship to the atomic weights or atomic volumes of their elements. The property is clearly not additive, nor would one expect it to be so.



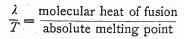
On the other hand a number of well-known thermodynamic relations involving the latent heat of fusion, e. g., Van't Hoff's freezing point formula, Thomson's pressure formula and the general relation.

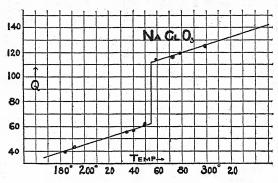


<sup>1</sup> Planck, Thermodynamik, 2d ed., p. 144.

are well established, and data like the above are necessary for the applications of these formulæ to specific cases. An example will be considered below.

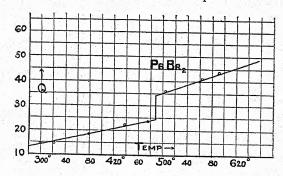
The values of the ratio





Plot 10.

given in column six are seen to be greater than four, with the exception of that for silver bromide for which the ratio is 3.4. Roozeboom 1 has shown that four is a unique value for this ratio,



Plot 11.

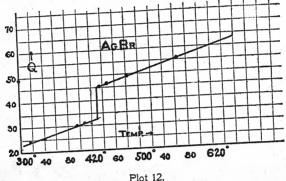
in that all substances for which the ratio is greater than four, give ideal melting point curves for their dilute solutions, which are concave to the axis of concentrations.

Specific Heat in the Solid State. — For our knowledge of specific

1 Heterogene Gleichgewichte, II., pp. 274 et seq.

heat relations of substances in the solid state we have to thank in the first instance Dulong and Petit, and later Regnault, and especially Kopp. Thanks to the two last named investigators we possess considerable reliable data on the mean specific heat of inorganic salts between about 50° and room temperature and 100° and the same temperature.

These data afford a sufficient verification of the general validity of Kopp's law, with however, certain pronounced exceptions. atomic heat of most elements is shown to be about 6.4, for oxygen



4.0, for carbon 1.8, etc., these values holding for temperatures below 100°. Since the specific heat of solids in general increases with rising temperature, we should expect if Kopp's law holds at the higher temperatures of our investigation that the atomic heats would possess corresponding higher values. This we find to be the case.

Thus if we except those compounds containing oxygen, which at lower temperatures are found to have an abnormally low atomic heat, the average atomic heat for the elements in the chlorides and bromides investigated is 7.1, this value holding for temperatures from about 430° to 500°, the melting point of the salts. Thus we have

$$AgCl = 14.3$$

$$TlCl = 13.9$$

$$AgBr = 14.2$$

$$TlBr = 14.6$$

$$Average = 14.2$$

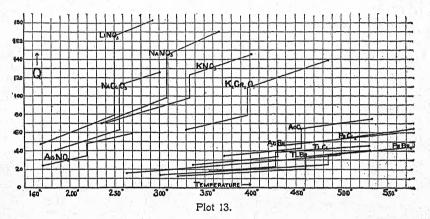
Therefore atomic heat of Ag, Tl, Cl and Br is 14.2/2 = 7.1. Again

$$PbCl2 = 21.6$$

$$PbBr2 = 20.8$$
Average 21.2

Therefore atomic heat of Pb, Cl and Br = 21.2/3 = 7.1.

The atomic heat of these elements increases therefore by over 10 per cent. for a rise of temperature of about 400° C. It is hoped that a more detailed investigation of the variation of the specific heat with the temperature for substances of the above type may be undertaken in the near future.



The molecular heats of the four salts containing five atoms in the molecule agree less well than those just considered, but it should be noticed that they are not all referred to even approximately the same temperature as the melting points of the several salts vary between wide limits. Omitting lithium nitrate, which is so hygroscopic that the data on it are believed to be much less reliable than those on the other salts, and assuming the atomic heat of potassium, sodium and nitrogen to be that just computed, namely, 7.1 (probably somewhat too high for the lower temperatures in question), we have from the data

$$KNO_3 = 29.5$$
 $NaNO_3 = 33.0$ 
 $AgNO_3 = 33.2$ 
 $NaClO_3 = 32.4$ 
 $Average = 32.0$ 
 $2 \times 7.1 + 3O = 32.0$ 

the equation, from which the mean value of the atomic heat of oxygen is calculated to be 5.9. With this value we may calculate the molecular heat of potassium bichromate  $K_2Cr_2O_7$  as follows:  $4 \times 7.1 + 7 \times 5.9 = 69.7$ . The observed value is 68.3 which is in better agreement with the computed value than the precision of the data would warrant one in predicting.

Specific Heat in the Liquid State. — The specific heat in the liquid state of each salt investigated was found in every case to be greater than the specific heat of the salt in the solid state. This is in accord with the few previously obtained data on the specific heat of the same substance in the liquid and the solid state. Thus the specific heat of solid mercury is 0.0319, of liquid 0.0535; solid bromine 0.0843, liquid 0.1109; of ice 0.48, and of water 1.0. The most marked increase in the value among the salts which we investigated is in the case of lead chloride and bromide and the still more complex salt potassium bichromate. The nitrates show the least change. The great increase (over 100 per cent.), observed in the specific heat of water in passing from the solid to the liquid form as compared with the slight increase observed in mercury, is probably to be attributed to a far greater change in the molecular condition of the former substance in changing state than in the latter. It seems not unreasonable to assume that the change in the value of the specific or molecular heat of a substance will be less, the less the change in its molecular structure as it passes from the one state to the other. Hence the relatively small increase in the specific heat of the salts investigated as they pass through their melting point from the solid to the liquid condition points to a relatively slight change in their state of association or dissociation. marked increase in the electrical conductance of these salts would therefore on this supposition be due not to an increase in dissociation but to an increase in migration velocity of the ions present resulting from the enormously increased fluidity of the molten salt.

The fact that the specific heat of aqueous solutions of inorganic salts cannot be computed from the specific heat of water and of the solid salt<sup>1</sup> indicates that when the salt passes into a highly ionized state as a result of solution, its heat capacity changes, in general

1 Ostwald, Lehrbuch, Vol. I., p. 602.

decreases, since the observed molecular heat of a solution is less than the calculated value. How large a part the now established phenomenon of hydration of the ions may play in producing this effect is open to question. Reasoning by analogy however from the results on solutions, one would naturally conclude that ionization of a salt tended to diminish its heat capacity rather than to increase it.

RECENT INVESTIGATIONS ON RELATED SUBJECTS PARTICULARLY WITH REFERENCE TO THE DEGREE OF IONIZATION OF FUSED SALTS.

Recently there appeared an article by Plato <sup>1</sup> in which he describes measurements of the latent heat of fusion of several salts of high melting point such as sodium chloride and barium chloride, by a modification of Tamman's cooling curve method, together with measurements of the lowering of the freezing point of these salts due to the addition of small quantities of a second salt. Some very interesting results were obtained, which, however, permit of quite a different interpretation to that given by the author.

Plato calculates the normal lowering of the freezing point due to one mol of solute in 100 mols of solvent according to Van't Hoff's formula

$$\Delta t = \frac{RT^2}{M_0 L_0} \frac{N}{N_0}$$

and compares the observed with the calculated value. The results which he obtained are given below.

	Solvent.	Solute.	Calculated Depression.	Observed Depression. t° C.
7.5	KCI	KF	3.4	3.2
	NaCl	NaF	3.2	3.4
	KF	KCl	4.1	4.0
	NaF	NaCl	4.1	3.4
	BaCl <sub>2</sub>	BaF <sub>2</sub>	5.3	14.4
	SrCl <sub>2</sub>	SrF <sub>2</sub>	6.4	11.6

For the first four salts, the observed depression is substantially equal to the normal calculated value from which he concludes that the degree of dissociation is very small. Since in the case of BaCl,

<sup>1</sup> Zeit. Phys. Chem., 58, 350, 1907; 55, 721, 1906.

and BaF<sub>2</sub>, the solute presumably splits into three ions, and since the observed depression is nearly three times that calculated, Plato further concludes that in this case the solute is nearly, complete dissociation.

Before discussing these conclusions further, we would call attention to a theorem first demonstrated by Stortenbeker, anamely, that the active mass of a liquid phase AB, dissociating into components A and B, is not changed by the addition of a small quantity of A or of B, and it will therefore remain in equilibrium with solid AB without change in freezing point, after the addition of small quantities of either A or B.

A shorter proof of this theorem, recently published by Lewis <sup>2</sup> is based upon the following equation, thermodynamically deduced by Duhem, for the change in active mass of various constituents of a mixture with change in active mass of any one of them:

$$\left\{ \frac{N_1 \partial ln \hat{\xi}_1 + N_2 \partial ln \hat{\xi}_2 + N_3 \partial ln \hat{\xi}_3 + \cdots}{\partial N_1} \right\} = 0, \tag{I}$$

in which  $\xi$  is the active mass of the component whose molal concentration is N. For a fused salt such as KCl for example this equation becomes

$$\left\{ \frac{N_{K}\partial ln\xi_{K} + N_{Cl}\partial ln\xi_{Cl} + N_{KCl}\partial ln\xi_{KCl}}{\partial N_{Cl}} \right\}_{p.t.} = 0.$$
 (2)

From the mass law

$$\frac{\xi_{K} \times \xi_{CI}}{\xi_{KCI}} = C \text{ (constant)}. \tag{3}$$

Hence taking the logarithm of both sides of (3) and differentiating we have

$$\partial \ln \xi_{\rm K} + \partial \ln \xi_{\rm Cl} = \partial \ln \xi_{\rm KCl}. \tag{4}$$

Since K and Cl in this case are the products of dissociation of KCl, it follows that

$$N_{K} = N_{CI}. (5)$$

Combining (2), (4) and (5), we have

$$N_{K}\partial ln\xi_{KCI} + N_{KCI}\partial ln\xi_{KCI} = 0$$
 or  $\partial ln\xi_{KCI} = 0$ , (6)

<sup>&</sup>lt;sup>1</sup>Zeit. Phys. Chem., 10, 183, 1892.

<sup>&</sup>lt;sup>2</sup> Proc. American Academy, October, 1907.

that is, the activity of the active mass of the liquid KCl is not changed by the addition of a small amount of K (or Cl) and it will therefore remain in equilibrium with solid KCl without change of freezing point.

Applying this theorem to the experimental results of Plato, we find just what theory would lead us to expect in the case of the addition of a small amount of KF to KCl, and other salts of the same type. The common ion does not lower the freezing point of the solution, while the sum of the concentrations of the other ion and of the undissociated portion of the solute is constant and equal to the concentration of the salt added, independent of its degree of ionization. Hence the freezing point lowering should be proportional to the total concentration of added salt, as observed. requires, however, that the solvent itself, e.g., fused potassium chloride, be highly dissociated, for the more it departs from the state of complete dissociation the less will be the concentration of the K ions due to it, and hence the greater the tendency of the K ions coming from the solute (e.g., KF) to change the active mass of that component. Thus it appears from Plato's results, that the lowering of the freezing point due to an addition of as great an amount as 3.5 mols NaF to 100 mols of NaCl (and corresponding concentrations for the other salts) is still normal, indicating that the concentration of Na ions in the fused solvent NaCl must be very great. In other words, the results point to a high degree of dissociation of the pure fused salt.

In the case of the addition of barium fluoride to barium chloride and similar combinations, Plato's results are so discordant (owing doubtless to uncertainty in the values of the latent heats of fusion) that very definite conclusions cannot be drawn. Combinations of binary salts offer, however, further evidence as to the order of magnitude of the dissociation of the fused solvent. This point was first called to our attention by Dr. Bray of this laboratory. Consider, for example, the lowering of the freezing point of fused lead chloride due to the addition of a small amount of lead bromide. The common Pb ion of the PbBr<sub>2</sub> would here again be inactive in lowering the freezing point if the solvent were highly dissociated into Pb and Cl ions; but in this case there would be two Br ions for every

equivalent added and hence twice the normal lowering would be expected if the degree of dissociation of both solvent and solute were complete. To test this prediction we determined the approximate freezing point lowering with these two salts, using a sensitive thermoelement for a thermometer. Temperature differences of 0.05° could be readily measured.

TABLE III.

Gms. PbCl <sub>2</sub> .	Gms. PbBr <sub>2</sub> .	Calculated Depression.	Observed Depression.	Ratio
17.8	0.199	1.95	3.°14	1.63
32.9	0.403	2.15	3.67	1.71
39.9	0.322	1.42	2.44	1.70

These few approximate measurements serve to differentiate this type of combination from that of a common ion with univalent salts, and make it very probable that the solvent is highly dissociated.

The results published in a recent paper by Foote & Levy 1 also bear out the above conclusions. These investigators dissolved small quantities of a series of salts having one ion in common with the solvent in sodium chlorate and determined the resulting lowering of the freezing point. The value of the latent heat of fusion of sodium chlorate obtained by them was 48.4 calories, as against 40.6 obtained by us. With this value they calculated the normal lowering of the freezing point for this solvent, and the molecular weight of the various solutes studied, by the usual Van't Hoff formula. The molecular weights calculated in this way, agree very closely with the normal molecular weights for concentrations as great in some cases as 10 per cent. (by weight). The agreement we find is even better if our value of the latent heat of fusion of sodium chlorate is used. In this case the differences between the observed and calculated molecular weight do not exceed a few per cent. for the following solutes: NaCl, NaNO, NaBr, Na, CO, Na<sub>2</sub>CrO<sub>4</sub>, NaF, KClO<sub>3</sub>, CsClO<sub>3</sub> and Ba(ClO<sub>3</sub>)<sub>2</sub>, all of which possess a common ion with the solvent sodium chlorate.

From these results the authors conclude that there is no polymerization. They point out that the data give no clue to the degree of dissociation, but conclude that neither solvent nor solute

<sup>&</sup>lt;sup>1</sup> Am. Chem. Jour., 37, 494, 1907.

can be approximately completely dissociated, for in that case, they say, there would result the same lowering of freezing point whether KNO3 or NaNO3 be added to NaClO3. Measurements showed, however, that the lowering with KNO3 was twice as great as with NaNO3. According to the above deduction, however, this is what should occur if the solvent and solutes are highly dissociated. For from each molecular weight of NaNO3 or KNO3 added, there would be formed two mols of ions, and if the solvent NaClO3 is highly dissociated into Na and ClO3 ions, the common Na ion from the NaNO3 will not tend to lower its freezing point appreciably, while the K ion from the KNO3 will, and hence the lowering should be twice as great in the latter as in the former case. This is what Foote & Levy find to be the case, and hence their results also substantiate our conclusion that pure fused salts are probably highly dissociated.

### · SUMMARY.

- 1. A method and apparatus were devised for measuring the latent heat of fusion of substances melting up to about 600° C.; this constant was determined for the following salts: KNO<sub>3</sub>, NaNO<sub>3</sub>, LiNO<sub>5</sub>, AgNO<sub>3</sub>, AgCl, TlCl, PbCl<sub>2</sub>, AgBr, TlBr, PbBr<sub>2</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and NaClO<sub>3</sub>.
- 2. The specific heats of these salts at temperatures just above and just below their melting points were also determined.
- 3. Kopp's Law was found to hold for these substances, but with an atomic heat at the temperatures employed of 7.1 instead of 6.4, for all of the elements investigated with the exception of oxygen.
- 4. The atomic heat of oxygen was found to be abnormal as it is at lower temperatures, with a value of 5.9.
- 5. The specific heat of all salts investigated is slightly greater for the liquid than for the solid state.
- 6. No stoichiometrical relations were apparent between the values of the latent heat of fusion, and the molecular, atomic or crystallographic properties of the salts investigated.
- 7. The values of the latent heat of fusion of certain salts were used to calculate the theoretical lowering of the freezing point of the salts due to the solution of a small quantity of a second salt. These values were compared with values observed by other inves-

tigators. A discussion of the results indicates that the pure fused salt and the dissolved salt are probably both highly dissociated.

8. The lowering of the freezing point of lead chloride due to small additions of lead bromide was approximately determined and the results compared with the theoretical lowering calculated from the latent heat of fusion of lead chloride. The results again point to a high degree of ionization of both solvent and solute.

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# AN EXPERIMENTAL STUDY OF PHOTO-ACTIVE CELLS WITH FLUORESCENT ELECTROLYTES. I.<sup>1</sup>

By PERCY HODGE.

THE effect of light on the electrical conductity of cells containing a fluorescent electrolyte has been studied by several experimenters, with somewhat conflicting results.

Cunningham<sup>2</sup> observed a small increase of conductivity in the case of uranyl nitrate when illuminated by the light from an arc lamp, but he states that no precautions were taken to protect the cell from the heat of the arc, and that therefore his results are not trustworthy.

Regner<sup>3</sup> also experimented upon solutions of eosin and fluorescein in water. His cell was so arranged that the liquid was in constant motion past the electrodes, and thus the danger of error from heating of the electrodes or liquid was largely eliminated. He was unable to obtain a change of conductivity as great as 0.1 per cent. in either case.

Nichols and Merritt <sup>4</sup> tried the effect of light upon five different fluorescent compounds, using, instead of water, absolute alcohol as the solvent, and obtained effects ranging from 0.05 per cent. increase of conductivity in the case of naphthalin-roth, to 1.1 per cent. in that of eosin.

Still more recently Camichael<sup>5</sup> has obtained a series of entirely negative results, and suggested that the precautions taken by the last named experimenters against heat effects were not sufficient, and that the change of conductivity observed by them was probably due to this cause.

<sup>&</sup>lt;sup>1</sup>A summary of the work described in this paper was presented to the Physical Society at the Washington meeting, April 24, 1908, and an abstract was published in the Physical Review, Vol. 26, p. 540, June, 1908.

<sup>&</sup>lt;sup>2</sup> J. A. Cunningham, Proc. Camb. Phil Soc., Vol. II., 1902.

<sup>&</sup>lt;sup>8</sup> V. K. Regner, Phys. Zeit., Vol. 4, 1903.

<sup>\*</sup>PHYS. REV., Vol. 19, 1904.

<sup>&</sup>lt;sup>5</sup> M. C. Camichael, Jour. de Phys., Vol. 4, 1905.

As the question seemed still to be an open one it was suggested to the author by Professor Nichols and Professor Merritt that he undertake a series of experiments which would, if possible, give conclusive evidence as to whether there is a conductivity change accompanying the phenomenon of fluorescence or not.

The author's experience in this line of work had been very slight indeed, up to the time of undertaking the above problem. Therefore he though it advisable to first repeat, as nearly as possible, some of the experiments of Nichols and Merritt, and afterward to go on from that point to a systematic and thorough study of the subject.

The substance first chosen for experiment was eosin, and nearly all the results to be described in the following paper were obtained with this substance. As solvent absolute alcohol was used, and in most cases the solution was saturated at room temperature.



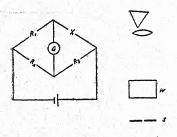


Fig. 1.

The apparatus used by Nichols and Merritt, and described by them in their article, was copied by the author as nearly as possible in the first experiments, various modifications being made from time to time as the work proceeded.

The essentials of the apparatus are shown in Fig. 1. The source of light A was a Schuckert arc lamp enclosed in the light tight cover which is used with the lamp for projection. After passing through a pair of condensers the beam of light illuminated the slit S, then went to a water cell W, and thence to a lens and crown glass prism, finally forming a spectrum on the front

of the light tight box D, containing the cell C. D was provided with a sliding front by which the light could be admitted to the cell C.

For measuring the change of resistance an ordinary Wheatstone bridge was used, the cell being placed in one arm, and the source of current being a battery of gravity cells, the number of which was varied as will be seen later. A very sensitive Sullivan d'Arsonval galvanometer was used with the bridge, the resistance of which was 1,100 ohms. The galvanometer was fitted with a concave mirror of four feet focus, and its constant with the scale at that distance was  $90 \times 10^{-11}$  per mm. deflection.

The cell used to contain the solution was a small rectangular glass cell 6 cm. deep and 1 cm. from front to back on the inside. In this were placed side by side, and at a distance of approximately a millimeter apart, two strips of platinum foil 0.1 mm. in thickness, 5 cm. long, and 3 mm. wide. Behind these in the cell was placed a piece of plate glass, holding the electrodes pressed against the front wall of the cell, and itself held in place by brass springs between it and the rear wall of the cell. A section of the cell is shown in Fig. 2, the thickness of the electrodes and other dimensions of the cell being considerably exaggerated. The dispersion of the prism used gave a visible spectrum at the point where the cell was placed about 4 cm. wide. Thus the portion of the spectrum illuminating the narrow space I mm. wide between the elec-

trodes was quite small, and it was easy to select the part of the spectrum producing maximum fluorescence without including the rays of longer wave-length which would be likely to produce

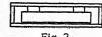


Fig. 2.

heat disturbances. In the case of the eosin cell the light used was at the infra edge of the green.

The fact was recognized, as had been done by Nichols and Merritt, that polarization effects would make it impossible to obtain the true resistance of the cell, and would at the same time greatly reduce the sensitiveness of the indications of change of conductivity due to light. Nevertheless the method in which a direct current was used was found to give much greater sensibility than any of the alternating current methods, and was therefore used, as an indication of a change of resistance was the chief thing to be looked for.

When the cell was first set up great difficulty was experienced in obtaining a balance, the drift toward higher values of the resistance being quite rapid and continuing for several hours.

at first thought to be due entirely to polarization, but it was found that if the top of the cell was covered so tightly that evaporization was prevented the drift lasted for only a short time, after which a comparatively steady condition was reached, and quite accurate measurements were possible. At no time was the cell absolutely free from a very slow drift, always toward higher resistance, and probably due partly to polarization and partly to a very gradual decomposition of the electrolyte. Evidence of the latter was seen in a very narrow strip of colorless liquid which was observed along the inner edge of the anode after several hours of application of the current. On account of this decomposition most of the tests were made with cells which had been freshly set up, the electrodes being removed and carefully cleaned between each two of the sets of tests.

The method of the experiment was as follows. After the apparatus had been set up and the cell placed in its dark box the slide was raised and the cell so adjusted in the spectrum that the liquid between the electrodes became brilliantly fluorescent. The slide was then dropped, shutting off the light, and a balance obtained with the bridge. In the measurements to be described in the first part of this paper the resistance of R, (see Fig. 1) was in nearly every case 10,000 ohms, that of  $R_8$  was 50,000 ohms, and  $R_4$  was adjusted to suit the resistance to be measured. As it was impossible to set the electrodes at exactly the same distance from each other when the cell was set up at various times the apparent resistances differed from each other greatly during different sets of readings. Also the polarization E.M.F. in the case of eosin was found to be over two volts. Therefore when two gravity cells were used the resistance was much higher than when four were used. When the applied E.M.F. was two volts the resistances ran between two and three thousand ohms. The sensibility of the bridge, of course, varied with the magnitude of the cell resistance, and when readings were being taken the sensibility was frequently tested by reading the deflection of the galvanometer produced by changing the variable arm by a known amount.

After the cell had stood in darkness long enough to obtain a fairly steady condition of the bridge, the slide was suddenly removed and the cell illuminated.

With two volts as the applied E.M.F. the result was an immediate and very large decrease of resistance, the amount of resistance change required in the variable arm to restore a balance indicating as high as ten or fifteen per cent. increase of conductivity. When the light was shut off the cell returned immediately to nearly the same resistance which it had before illumination. The test was repeated many times and on different days, and always with about the same results. As the effect was vastly larger than any that had been anticipated it seemed advisable to see if it could in any way be due to heating of the liquid. With this end in view the temperature coefficient of the solution was determined in the following manner. A balance was obtained at the temperature of the room. Then the cell was surrounded with ice water and a balance again obtained. Lastly the ice water was drawn off and the cell allowed to regain the temperature of the room. The first and last values of the apparent resistance were in turn subtracted from the second and then averaged. The result showed a temperature coefficient between zero and 20 degrees of not more than 1.5 per cent. per degree. The effect of the light was also tried while the cell was in ice water and found to be apparently about as large as at room temperature. These tests seemed to preclude the possibility of any considerable portion of the effect being attributable to heat. An additional reason why the effect should not be attributed to heat was mentioned by Nichols and Merritt in their article, namely, the fact that the change of conductivity took place within an exceedingly short time after the light was thrown on the cell, and after the light was shut off the cell immediately resumed its former state. This fact was confirmed by the author's experiments, the time required for the change to take place being apparently considerably less than a second, and the decay of the effect taking about the same time.

The next step in the work was a series of tests with the same cell and solution, but using four gravity cells in series as the source of E.M.F. A difference of effect from that obtained with two cells was expected, as with two cells only a very small current could possibly have passed through the cell since the applied E.M.F. was not equal to the E.M.F. of polarization, while with four volts the current flowing was of considerable magnitude. The effect anticipated

was one similar to the first but of smaller magnitude. When the light was thrown on the cell, however, the surprising result was obtained of a large *increase* of resistance instead of a decrease as in the former experiments. The effects were produced as promptly as those of the preceding experiments and died away nearly as quickly.

Here was something quite puzzling, and which apparently contradicted any theory that might be advanced in regard to the first effect. If the remarkable decrease of resistance observed in the first experiments was due to electrons set free by ionization of the solution accompanying the phenomenon of fluorescence it seemed highly improbable that an increase of resistance would be produced by light under any conditions whatever. Further, both effects were entirely too large to be satisfactorily accounted for by any theory analogous to that applied to the ionization phenomena in gases, phenomena which it might be supposed would very probably accompany fluorescence.

Again, if the decrease of resistance in the first case were due to ionization of the nature of that produced in gases, it should be greater in dilute solutions than in concentrated, since, owing to the greater penetration of the light into a dilute solution the number of molecules affected would be as great as in a concentrated solution, while, owing to the greater distance between the molecules, the mean free path of the ions would be greater and therefore recombination less rapid. A number of experiments were made by diluting the saturated solution with two, four and six parts by volume of alcohol, and the effects were found to be diminished, even in the solution with two parts of alcohol, to not above a change of I per cent. in resistance.

In order to vary the conditions it was thought worth while to try next a cell in which, as in Regner's experiments, the liquid could be kept moving past the electrodes while being illuminated. All possible heat effects would be in this way eliminated, and some light might by thrown upon the nature of the phenomena which would not be brought out when the liquid was at rest. A cell was therefore prepared in the following manner, again copying the design of one used by Nichols and Merritt.

A glass tube of 5 mm. internal diameter was drawn down at its

middle point to a capillary about a millimeter in outside diameter and 1.5 cm. in length, Into the larger parts of the tube, at either end of the capillary were led platinum wires in the form of spirals to serve as electrodes. The upper end of the tube was attached to a tubulated bottle to serve as a reservoir for the liquid. To the lower end of the tube was attached a capillary tube to hold the liquid back and keep the capillary full. With this apparatus the liquid could be illuminated while flowing through the capillary at any rate desired. A number of tests were made with the appa-

ratus, and in all cases the results were entirely negative. The form of the cell was such, however, that its resistance was much larger than that of any of the cells



Fig. 3.

previously tried, and as the sensitiveness of the bridge was much less under these conditions than when the resistance was less, the results were looked upon with some suspicion.

Another form of circulation cell was therefore devised which was free from the above objection.

A piece of glass tubing was obtained from the Taylor Thermometer Co. of Rochester, whose internal cross-section was almost that of a figure 8, except that where the two loops of the eight would cross one another there was an opening between them about 0.3 mm. in width. In a short length of this tubing were placed two No. 16 platinum wires, each having a length of five centimeters. The wires were parallel to one another in the two loops of the 8, and from the end of each a small platinum wire was led out through the walls of the tube. There was thus left (see Fig. 3. which shows an enlarged cross-section of the cell) a narrow space between the electrodes through which the liquid could flow, the electrodes themselves almost filling the loops of the 8. Below the electrodes the tube was drawn down to a coarse capillary to make it possible to keep the space between the electrodes filled with liquid, and the upper end of the tube was attached to a tubulated bottle as in the last experiment. By illuminating the contracted part of the tube between the electrodes a moving strip of liquid about 0.3 mm. wide and 0.1 mm. from front to back could be excited to fluorescence, while the current flow was from side to side of the strip at right angles to its length.

Upon connecting the cell to the bridge it was found that its resistance reached a steady value almost immediately after the current was turned on, and retained the same value as long as the motion of the liquid continued.

The movement of the liquid was quite rapid, the time required to empty the 400-c.c. reservoir being about ten minutes. As the whole space between the electrodes could not have held more than o.r c.c. a complete change of liquid between the electrodes could not have occupied more than a fifth of a second.

Numerous tests were made with this apparatus, but in no case was there any evidence of a change of conductivity while the liquid was in motion. When, however, the lower end of the tube was stopped the effects reappeared, though they were not as marked as in the original type of cell. The sensibility of the bridge as used in these tests was at least 0.01 per cent. Therefore it seems fair to conclude that there could not have been any appreciable effect due to electrons set free at the instant fluorescence began in any part of the liquid, unless this effect required a considerable time to make itself known. Unless the free electrons traveled very slowly indeed it would seem likely that some of them at least would reach the electrodes and produce greater conductivity, even when the liquid was moving as fast as in the above experiments.

Attention was next given to the study of the effects at the two electrodes separately and to the liquid between them, to find out, if possible, just where the phenomena took place which caused the conductivity changes.

As nothing but negative results were to be obtained from a circulation cell the original type of cell was again adopted, and in the front of the box D of Fig. I was placed a screen with a vertical slit cut in it about 4 mm. wide. By placing the cell behind this screen in such a manner that only one electrode could be seen from the front of the box through the slit, it was possible to observe the effect of illuminating one electrode at a time, the other being in darkness behind the screen. With this arrangement and two gravity cells the effect was tried on anode and kathode in turn. When the anode was exposed the effect was very small, while on the contrary when the kathode was exposed the effect was found

to be about as large as when both were exposed. As some of the liquid between the electrodes was illuminated in either case it was not certain whether the effect was produced only at the electrode or whether the liquid at a distance from the electrode also played its part in it. Therefore the question as to what would happen when the electrodes were both covered and the liquid between them exposed had next to be settled.

To this end several different arrangements of the cell were tried. The first tests were with the same electrodes which had been used in the earlier type of cell, but in front of each of them was placed a thin strip of hard rubber 0.15 mm. thick, projecting just beyond the platinum strip so as to completely screen it from the light, but so as to leave about eighty per cent. of the liquid between the electrodes exposed to the light.

With this arrangement no effect could be obtained by illumination. However, it was felt that the test was not very conclusive as the total thickness of the film of liquid acting as conductor between the electrodes was that of both the electrode and the rubber strip, and as the absorption coefficient of a saturated solution of eosin is very large it was not at all certain that the whole thickness of the layer was illuminated, so as to be fully excited to fluorescence.

In order to overcome this difficulty another type of cell was constructed after the following manner:

A block of hard rubber was sawed of such shape and size as nearly to fit the rectangular cell used in most of the experiments.



Fig. 4.



Fig. 5.

The block was then clamped to another block of ebonite and with a 3%-inch drill two holes were bored between the blocks in such a manner as to leave in each block a pair of grooves of semi-circular cross-section, and separated from each other by a narrow strip approximately 2 mm. wide. The block that had been sawed to fit the cell was then placed in the cell and two L-shaped electrodes placed in the grooves in the positions shown in Fig. 5, which illustrates a

section of the cell with block and electrodes in place. It will be seen from the figure that the electrodes hold the ebonite block back from the front wall of the cell so as to leave a film of liquid of the thickness of the platinum strips between the two grooves when the cell is filled with liquid. The electrodes themselves in this cell offered a broad conducting surface, while being entirely away from the thin film of liquid between the grooves. This film could be perfectly illuminated, was isolated from the electrodes, and at the same time included a large part of the total resistance between the electrodes.

Careful tests were made with this cell and the results were entirely negative, though the resistance of the cell was quite low compared with others that had been tried, averaging about 40,000 ohms with saturated solution, and the sensibility of the bridge was as high as 0.005 per cent. Also the condition of the cell within a few minutes after it was set up was very steady indeed, and a slight change of conductivity would have been readily detected.

In addition to the saturated solution a solution of five parts alcohol to one of saturated eosin solution was tried with both two and four volts E.M.F., but likewise with entirely negative results. From the results of these last experiments the author was convinced that a change of conductivity in the liquid itself, except at or very near the electrodes, did not take place when fluorescence was produced.

Attention was therefore given to the phenomena at the electrodes themselves.

It had frequently been observed that, however smooth the strips of platinum were when they were placed in the cell, and however tightly they were clamped against the front wall, when the solution was poured in a thin film of liquid immediately crept up between the electrodes and the front wall of the cell. There seemed, therefore, to be two regions in which the effects might be produced, either at the inner edges of the electrodes or in the region in front of the electrodes or in both places at once.

From a variety of minor indications which had been noticed from time to time the author was convinced that the main effect was to be looked for in the thin film and not at the edges of the electrodes. In order to test the matter the effect was first tried of placing thin

strips of ebonite in front of the electrodes as in one of the previous experiments, but instead of covering the electrodes the ebonite strips were only allowed to cover the extreme outer edges of the platinum strips, thus leaving nearly the whole of the electrodes exposed to the light, but behind a layer of liquid a number of times as thick as the capillary film formed when the electrodes were against the front wall of the cell. The change of conductivity, though still present, was found to be very greatly diminished.

As mentioned in connection with a previous experiment, the reduction of the effect might easily have been due to the absorption of the light by the thick layer of liquid in front of the electrodes so that fluorescence did not occur very near the surface of the platinum strips.

A second arrangement was then tried in which the platinum strips were separated from the front wall of the cell by strips of lantern slide cover glass a millimeter in thickness. The inner edge of each electrode (see Fig. 5) was allowed to project slightly beyond the edge of the glass.

Thus the capillary film between the electrode and strip of cover glass could be illuminated while the inner edge of the electrode was completely screened from the light by a thick layer of liquid. When the light was turned on this cell the effects were found to be present in as great a degree as when the whole of the electrode had been illuminated.

Lastly the platinum strips were again placed against the front wall of the cell and the inner edges covered while the rest of the electrodes was illuminated. Again the effect was present, as was to be expected.

The conclusion arrived at from the various tests was that, in the first place, no effect is produced by light upon the conductivity of a fluorescent solution unless a region very near the electrodes is illuminated and that further, this effect at the electrodes is only produced in a very thin film of the liquid immediately in contact with the surface of the plates.

It may be well to state at this point that, while no reference has thus far been made to a variation of the effects in different parts of the spectrum, frequent tests were made in all of the experiments described, to see if the effects could be produced by parts of the spectrum which did not produce fluorescence. In all of these tests the effects obtained were either very feeble or entirely lacking. Thus, in the red, where the energy of the arc is the greatest, but where no fluorescence was to be detected, no effects were observed which were as great as 0.2 per cent. either way. Thus the frequent references to fluorescence in connection with the effects observed seem entirely justified.

The next step undertaken in the investigation was a study of the variation of the effects at anode and kathode with varying potential difference at the terminals of the cell.

For this purpose the original form of cell was adopted, with electrodes 0.15 mm. thick and 3 mm. wide, placed next to the front wall of the cell and 3 mm. apart. The greater distance between the electrodes was adopted so that while one of the plates was being illuminated no stray light could reach the other electrode. The greater thickness of the electrodes was necessary in order to keep the resistance of the cell as low as possible, and in view of the results of previous work could not materially affect the sensibility of the cell.

The screen in the front of the light tight box D was so arranged that the cell could be moved into a position to expose either electrode to the light without having to raise the slide in the front of the box to make the adjustment.

As a source of E.M.F. a set of four sal-ammoniac cells was first used, but as these were found to drop slightly in voltage during a run, a pair of storage cells was substituted for them. The cells were connected to the ends of a rheocord, consisting of ten meters of manganin wire, and sliding contacts were arranged so that any desired potential difference could be obtained at the bridge terminals, up to the limit of the cells.

To the bridge terminals were also attached leads from a large Weston milli-voltmeter, a resistance being placed in a series with the meter, and the whole calibrated to a total range of 15 volts. With this arrangement it was found easy to obtain the potential difference between the terminals of the bridge with an accuracy of .01 of a volt, and any given value of the potential difference could

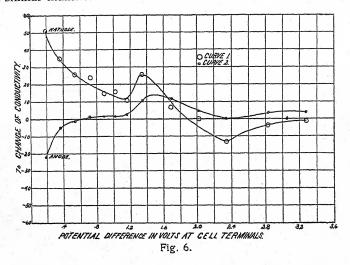
be maintained constant throughout the time needed for the readings.

For greater simplicity in computation, and to make it possible to maintain the potential difference between the terminals of the cell at a constant ratio to the voltmeter reading, the bridge arms were arranged as follows (see Fig. 1):  $R_3$  62,500 ohms,  $R_4$  10,000 ohms, and  $R_1$  a 100,000-ohm box to be used as the variable resistance. Thus, unless in a case where the resistance of the cell was so great that the 10,000-ohm box had to be varied, the fall of potential across the cell terminals was nearly 86 per cent. of the voltmeter reading.

The change of resistance due to the illumination was estimated in two different ways, depending on the magnitude of the effect. the galvanometer reading remained on the scale when the cell was illuminated, a reading of the deflection was taken, then the illumination stopped and a second reading taken and the two averaged. A plug was then inserted in the 10,000-ohm box, the change of galvanometer reading obtained, then the plug was removed, a second reading taken and the two averaged. Assuming that the galvanometer deflection was proportional to the change of resistance in the 10,000-ohm box, the number of scale divisions corresponding to a change of one ohm or one part in ten thousand was easily obtained. As increase or decrease in the apparent resistance of the cell would produce the same change in the potential difference at the galvanometer terminals as the same percentage decrease or increase of the resistance in  $R_{\rm a}$ , it was easy to get quite satisfactory estimates of the change produced by the illumination. If the effect of the light was great enough to throw the galvanometer off the scale, a balance was restored by changing the resistance in  $R_1$ . The light was then shut off and a second balance was obtained, and from the average of the two changes in R, the change of resistance of the cell was calculated.

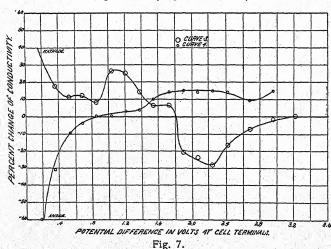
Curves were plotted, using potential differences at the cell terminals as abscissas, and change of conductivity, *i. e.*, reciprocals of resistance changes, as ordinates. Eight curves are shown in the accompanying figures. Each value of the conductivity change is the average of at least two readings, taken at intervals of five minutes

time. These curves are typical of a large number that were obtained in a similar manner.



Owing to the variation in the intensity of the arc light used, and to the difficulty of setting up the cells in exactly the same manner each time, the magnitude of the effects obtained varies considerably in different curves. Nevertheless the character of the effects obtained did not vary greatly.

In curves 1 and 2, 3 and 4 (Figs. 6 and 7) the kathode and



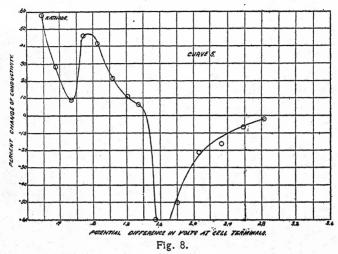
anode were illuminated alternately throughout the experiment. Each value of the change of conductivity is the average of at least two measurements, made at intervals of five minutes from the end of one measurement to the beginning of the next. It will be noticed that the kathode shows at low voltage a large decrease of resistance due to the light, followed by a considerable increase of resistance as the voltage rises. On the anode the effect at low voltage is just the opposite to that on the kathode and changes sign as the voltage rises as in the case of the kathode.

It will be noticed that the change of sign of the effect occurs considerably earlier in the case of the anode than in that of the kathode. The result of this is that for a considerable range of voltage both electrodes show a decrease of resistance with the light. As this region happens to include the voltage obtained when two gravity cells were used as the source of current, it is not surprising that a large decrease of resistance was observed in the first experiments, when both electrodes were exposed to the light at once.

As the curves showed that the effects on the two electrodes were in general of opposite sign, it was thought advisable to arrange a cell so that one electrode could be studied at considerable length, and with a certainty that no complications would be introduced by stray light reaching the other electrode.

In order to have the electrodes as far apart as possible, and still to keep the resistance of the cell within reasonable limits, the electrode to be exposed was alone fixed in the front of the cell, clamped to the front wall in front of and very near the edge of a narrow strip of glass. The other electrode was made L-shaped, nearly a centimeter being the length of each leg of the L cross-section. This electrode was placed in the main part of the cell with the base of the L toward the side of the cell away from the light source. This arrangement insured a very large electrode surface and also an average cross-section of the liquid between the electrodes sufficient to make up for the greater distance between them. It also served to concentrate the greater part of the resistance at the electrode to be illuminated.

As the kathode effect seemed the most promising for further study the current was sent through the cell from the large electrode to the one to be exposed. A number of runs were made with this cell and from the results curves were plotted, of which 5, 6, 7 and 8 are typical specimens (Figs. 8, 9 and 10). It will be seen that the effects are considerably greater than those obtained in the former experiments, and also that



the form of curve obtained is in general more regular than the others. The peculiar rise of the effect after the large decrease shown in the first part of the curve does not appear to be accidental, but is common to almost all the curves plotted for the kathode effect.

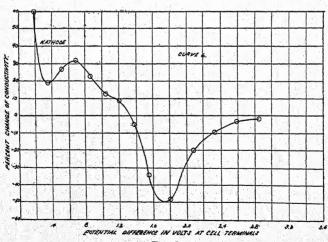
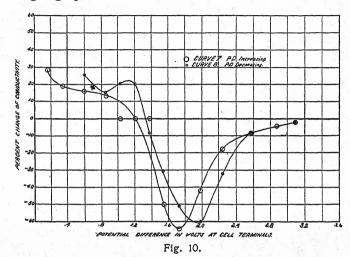


Fig. 9.

Curves 7 and 8 were made to ascertain the effect which the previous history of the cell might have on the action of the light. Curve 7 was obtained in the usual way, and immediately after a run was made, without changing the cell, but beginning with high voltage and reducing the voltage by the same steps that had been used in going up,



It will be noticed that the curves are very much alike, the one taken on decreasing voltage showing a slight shift toward the right. Also for the last two points on the return curve it was found impossible to obtain a balance of the bridge, the condition of the cell appearing very unstable. At the three voltages 1.03, 1.21 and 1.38 of the first of these two curves a phenomenon was observed which occurred frequently throughout the experiments, at the point where the effect reversed. When the cell was first exposed the galvanometer showed an immediate decrease of resistance, followed in a few seconds, with the light still on, by a large increase. When the light was shut off the cell showed the two changes in the reverse order.

This would seem to indicate, at least in this region, a combination of two effects, one growing to a maximum more rapidly than the other, and dying away more slowly.

A few experiments were made with fluorescein in absolute alcohol,

a trace of caustic soda being added to produce fluorescence. The effects obtained were very similar to those with the eosin, but not nearly as marked.

Rhodamin was also tried, with somewhat doubtful results, except that the effects with very low voltages were fully equal to those with the eosin.

Since there seemed to be no doubt that the seat of the effect was the thin film of liquid in front of the electrode, and since the current could not be supposed to flow only to and from this film and to neglect the opportunity to enter the edge of the electrode, it did not seem possible to account for the changes in resistance observed, except by the actual creation of an electromotive force at the surface of the electrode or near it, by the action of the light. If such an effect did exist it would account for the change of resistance when either anode or kathode was illuminated, so long as low voltages were used. For suppose the E.M.F. produced to be such as to tend to make the exposed plate positive to the unexposed one. Then if the exposed plate were made the kathode with regard to the outside E.M.F., the E.M.F. due to illumination would act with the original E.M.F., producing a greater current through the cell and making its apparent resistance, as measured on the bridge, less.

If, on the contrary, the direction of the impressed E.M.F. were reversed, the photo-E.M.F. would oppose the passage of the current and the apparent resistance of the cell be increased.

The reversal of the effects when the voltage was raised is not easy to account for. From a number of tests of the polarization E.M.F. of eosin cells, made by comparing the E.M.F. with that of a standard cell by means of a condenser, the effect of maximum polarization appears to be a back E.M.F. of over two volts. This value determines the point where any considerable current begins to traverse the cell, and hence it would be most natural to expect that just here would occur any marked change in resistance phenomena, such as the reversal of the illumination effect. This, however, does not seem to be the case, for it will be noticed from the curves that the reversal in the case of the kathode occurs at very nearly 1.7 volts. while at the anode the voltage is much lower. That the effects at high voltages are connected in some way with the polarization of the cell seems, nevertheless, most probable, though in what manner the author has not as yet been able to determine. If the light effect, through reduction of the electrolyte, is able to produce free hydrogen and thus increase the amount of polarization, it is still difficult to explain why the duration of such an effect should be only that of the illumination, dying away almost immediately when the light is shut off. Further work on that part of the problem has been postponed for the present.

Assuming that the effect at low voltage is due, as has been suggested, to a photo-E.M.F. similar to those which have frequently been observed in cells containing silver salts and many other electrolytes, the author next turned his attention to testing the effect of light on the cell when no external E.M.F. was applied.

The same type of cell was used as had been used for all of the experiments on the kathode alone. The terminals of the cell were connected directly to the Sullivan galvanometer which had been used with the bridge in all the previous experiments.

Very considerable effects were produced by the action of the light, ample in magnitude to account for the phenomena observed with the bridge at low voltages.

A series of experiments was then undertaken to find if in any way this photo-electric effect was intimately connected with fluorescence.

In the first place tests were made throughout the visible spectrum, and curves plotted showing the variation of the current produced in the galvanometer as a function of the wave-length of the exciting light. The effect was found to increase regularly from the edge of the visible spectrum in the violet to a pronounced maximum just before the absorption band was left in going toward the red, namely, just at the infra edge of the green. The decrease of effect from this point on toward the red was very sudden indeed, and the effect was entirely lost before the edge of the visible spectrum was reached. Three other substances, namely, rhodamin, fluorescein and naphthalin-roth were found to give similar effects, and in each one the maximum results were obtained at the infra edge of the absorption band. In rhodamin the effects were found to be enormously greater than with the eosin, but with the other two substances the results were less satisfactory.

With rhodamin tests were made by a condenser method to test the magnitude of the E.M.F. produced, and it was found to be as high as 0.2 of a volt. In eosin it is probable that the maximum was not over half that amount.

Dilute solutions of rhodamin were also tried with very good The maximum dilution thus far tested is that of one part saturated solution to ten of alcohol.

With dilute solutions of eosin, however, the effects were greatly reduced.

The extremely thin capillary film was found to be unnecessary, either in eosin or rhodamin, though the effects produced when the electrodes were more than 0.02 mm. back from the front of the cell were very small.

Tests were made of the absorbing power of both of the substances in saturated solution, and it was found that practically no light penetrated to a depth of 0.02 mm. in the region of the absorption band. Thus, if the effect is produced at the surface of the platinum plate itself, a film of this thickness or greater would completely screen the electrode from the action of the light.

While the author feels that he has wandered much in the dark, among a most confusing and complicated set of phenomena, he believes that the results thus far obtained are not entirely without value, and he hopes in the future to throw more light on the meaning of the effects. Also he believes it quite possible that he will be able to prove a definite connection between the photo-electric effects in fluorescent liquids and the phenomenon of fluorescence itself.

To Professor Nichols and Professor Merritt, under whose guidance this work has been done, the author is truly grateful, both for their many helpful suggestions and for their unlimited patience with his many questions.

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## SOME PHENOMENA OF THE PERSISTENCE OF VISION.1

By Frank Allen.

THE experiments to be described in this paper were suggested by some discussed in a communication to the Physical Review some years ago. A full description was there given of the method of measuring the persistence of vision which was first used by E. L. Nichols. The essential features of this method are few and simple. In front of the slit of the spectrometer is placed a sectored disk, which, when rotated by an electric motor, interrupts the light causing a flickering of the part of the spectrum under observation. By electrical means the speed of the disk is recorded on paper on a rotating drum, which enables the duration of a single flash of light upon the eye to be determined when the speed of rotation of the disk is such that the flickering just disappears. The duration of these light impulses varies with the luminosity of the spectrum, and, when plotted with the wave-lengths of the colors observed as abscissæ, gives a persistence of vision curve.

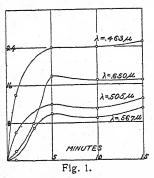
I. It was observed 3 that when the eye is protected from light by being blind-folded or by remaining in a dark room, the time of persistence of all color impressions was increased. Experiments were accordingly made to determine how this effect varied with the time of darkness adaptation. Observations of the persistence of vision were made on four colors, red, yellow, green and blue, after intervals of darkness adaptation of one, three, five, ten and fifteen minutes. The wave-lengths of the colors observed, and other measurements, are given in Table I. and the results are shown graphically in Fig. 1. For convenience in plotting, the ordinates are the differences between the normal readings and those made

<sup>&</sup>lt;sup>1</sup> Read before the Royal Society of Canada, May, 1908.

<sup>&</sup>lt;sup>2</sup> Frank Allen, Phys. Rev., Vol. XI., 1900, p. 257.

<sup>3</sup> Ibid., p. 265.

after the different intervals of adaptation. The adaptation curves



are of the "saturation" type, and show that, as far as the persistence of vision is concerned, darkness adaptation produces its maximum effect in about five minutes, the measurements after the ten and fifteen minute intervals showing no increase over those for five. There is, indeed, an indication in the curves of a partial return to the normal condition of the retina between the five and fifteen minute intervals of adaptation.

It will also be noticed that the maximum is least in the case of the brightest color used ( $\lambda = .567 \,\mu$ ), and greatest for the feeblest ( $\lambda = .463 \,\mu$ ).

- 1							201		
Adaptation.	100	-	Obs	servat	ion Color.				
Adaptation.	λ = .567 /	ι.	$\lambda = .505 \mu$	$\lambda = .65$		»μ. λ=		.463 μ.	
Time.	Persistence.	Diff.	Persistence.	Diff.	Persistence.	Diff.	Persistence.	Diff.	
Normal.	.0117 sec.	0	.0133 sec.	0	.0135 sec.	0	.0193 sec.	0	
1 minute.	.0117 "	0	.0139 "	6	.0137 "	2	.0206 "	14	
3 minutes.	.0124 "	7			.0143 ''	8			
5 "	.0127 "	10	.0145 "	12	.0153 "	18	.0216 ''	24	
10 "	.0126 ''	9	.0144 "	11	.0152 "	17	.0216 ''	24	
15 "	.0128 "	11	.0146 "	13	.0152 "	17	.0217 "	25	

TABLE I.

II. A similar series of curves was obtained after fatiguing the retina by exposure to light of certain definite hues. Readings of the persistence of vision were made after intervals of fatigue of one, two, three, five and ten minutes. Observations were made upon the same, or nearly the same, portions of the spectrum as the fatiguing colors. The measurements are shown in Table II. and are plotted in Fig. 2 according to a convenient scale of numbers so chosen that the curves are all exhibited in one figure. The zero of each curve, which corresponds to the normal persistence of the particular color, is the intersection of the curve with the axis of ordinates.

With all colors the fatiguing effect of the light stimulus reaches

its maximum in about three minutes, further exposure to light seeming to make no difference with the duration of light impressions.

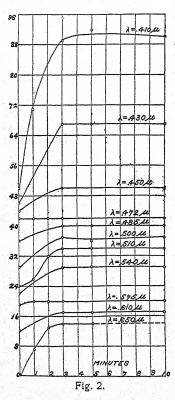
TABLE II.

	Ob	servation	Colon	I							
Time of Fatigue.	- 2	$\lambda = .650 \mu$ Satigue Co $\lambda = .675 \mu$	lor		б10 µ б10 µ			=•575 μ =•589 μ			
- unguo	Pers	sistence.	No.	Persiste	nce.	No.	Persis	tence.	No.	Persistence.	No.
Normal.	.01	36 sec.	0	.0123 s	ec.	12	.0118	sec.	19	.0125 sec.	22
1 min.	.01	43	7				.0119	•	20	1 10 1	1 1
2	.01	49	13				.0119	9	20	,	1,
3	.01	.50	14	.0128		17	.0119	9	20	.0132	29
5	.01	.50	14	.0128		17				.0132	29
10				.0128		17	.0119	)	20	.0132	29
	ОЪ	servation λ=.510 μ		λ=	.500 μ	- 1	λ=.485 μ			λ=.472 μ	
Time of Fatigue.	. 1	λ=.510μ Fatigue Co λ=.523μ	lor	λ=.	500 μ		λ=.485 μ		λ=.485 μ		ı.
z atiguo.	Per	sistence.	No.	Persiste	ence.	No.	. Persistence.		No.	Persistence.	No.
Normal.	.01	26 sec.	24	.0140 s	ec.	29	.0156	5 sec.	36	.0165 sec.	42.
1 min.	.01	28	26							.0165	42
2	.01	34	32	1					i	.0165	42
3	.01	36	34	.0148		37	.0160	)	40	.0165	42
5	.01	36	34	.0147		36	.0160	5	40	-	1
10	.01		34	.0148		37	.0160	)	40	.0165	42
Time (		λ Fat	vation ( =.410 \mu. igue Co =.413 \mu	lor			=.450 µ =.450 µ			λ=.430 μ λ=.430 μ	
		Persist	ence.	No.	Pe	rsiste	nce.	No.	Pe	rsistence.	No.
Norm	al.	.0334	sec.	50	.0225 sec.		44	.0	280 sec.	46	
1 min	ı.	.0355		71							
2											
3		.0373		89	.0	231		50	.0	301	67
5	1	.0376		92					.0	301	67
10		.0374		90	.0	231		50	.0	0301	67

Perhaps the most remarkable curves are those for the yellow and blue colors whose wave-lengths are .575  $\mu$  and .472  $\mu$  respectively. The latter of these is a straight line, and the former nearly so. For these colors the retina does not seem capable of being fatigued, as the duration of the color impressions always retains its normal value.

The differences between normal and maximum readings of the various curves vary in magnitude, and are shown in Fig. 3. This

curve is characterized by three elevations, corresponding to the red, green and violet of the spectrum, which are separated by two de-



pressions corresponding to yellow and blue of wave-lengths .575  $\mu$  and .472  $\mu$  respectively. It is noteworthy that these two depressions agree with the fundamental yellow and blue of the Hering theory of color vision, while the blue is nearly that chosen by Helmholtz and by König and Diderici (viz.  $\lambda = .470~\mu$ ) as one of their fundamental colors. The wave-lengths of the maxima of the red and green elevations also are the fundamentals of those colors which have been selected by the last two writers.

This curve with its three elevations seems to support the view that there are but three fundamental color sensations, which correspond to some hues of red, green and violet.

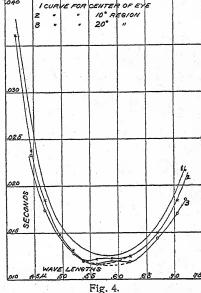
III. It was noticed from time to time that the persistence of color impressions was not constant over all parts of the retina. When no

flickering of the color under observation was perceptible in the center of the retina a slight movement of the eye in any direction, which allowed the light to fall upon the peripheral portions of the retina, was always sufficient to destroy the apparent continuity of the light.

To investigate this, a short piece of platinum wire, heated electrically so as to be just plainly visible, was placed in such positions, that, when viewed directly by the eye, the flickering light of the spectrum fell at determinate positions on the outlying parts of the retina.

Two sets of observations were made at two regions on the temporal side of the retina about ten and twenty degrees from the center.

Measurements were attempted at other regions farther out, but the results were too uncertain to be of any use.



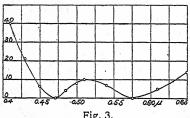


Fig. 3.

The measurements are shown in Table III. and are plotted in Fig. 4 in comparison with a curve for the center of the eye.

TABLE III.

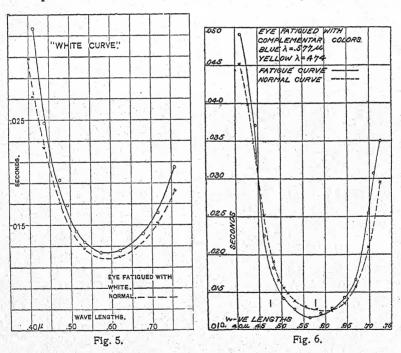
	1	Persistence.			Persistence.			
λ	Center of Retina.	10° Region.	200 Region.	λ	Center of Retina.	10° Region.	20° Region.	
.418 μ	.0372	.0361		.562	.0127	.0122	.0117	
.446	.0274	.0238	.0233	.588	.0126	.0123	.0120	
.472	.0196	.0185	.0174	.620	.0132	.0125	.0119	
.495	.0163	.0148	7 7 7	.670	.0158	.0150	.0144	
.520	.0141	.0132	.0128	.705	.0198	.0184	.0170	
.538	.0135	.0120	.0120	.720	.0220	.0216	.0185	

The curves show that the duration of all color impressions diminishes as the distance from the center of the retina increases; or, in other words, the peripheral portion of the retina is more sensitive to fluctuations in the intensity of the light than the center.

The ten and twenty degree curves show also a remarkable ele-

vation in the part corresponding to the yellow and greenish yellow. In direct vision the light rays fall upon the macula lutea or yellow spot where the greatest distinctness of vision occurs. This spot is, however, small and would not be stimulated by the light falling on the outer regions. As the lowest point of the persistency curve corresponds to the brightest part of the spectrum, the curves show that to the outer regions of the retina under consideration, the most luminous point of the spectrum is nearer the green than it is to the macula lutea.

An elevation in a persistency curve has always been found associated with some induced or natural abnormality of color vision. Here, however, it is found in the normal persistency curves for the outer portions of the retina, and indicates some slight modification



in the perception of yellow. The macula lutea contains a yellow pigment and no visual purple, while the retina in other parts has only the visual purple. This latter substance absorbs, and is bleached by, light of all parts of the spectrum but in amounts vary-

ing with the wave-length, the absorption being very slight in the red and greatest in the yellowish green, which has the most rapid bleaching effect. The region of the spectrum, therefore, which is most absorbed by the visual purple coincides with the elevations of the persistency curves.

IV. In the paper to which reference has been made an experiment was described in which a persistency curve was obtained when the eye was fatigued with white light from an electric arc. This curve and its comparison normal curve are shown in Fig. 5 which is reproduced from the paper cited.

As white light, indistinguishable from ordinary white, may be obtained by mixing two complementary colors, observations of the persistence of vision were made after fatiguing the retina with proper combinations of colors. Two overlapping spectra were formed with a Helmholtz color mixer and the selected complementaries combined in a shutter eyepiece. By means of nicol prisms in the collimators the intensities of the two spectra were adjusted until the narrow field of light in the eyepiece was white.

The first pair of complementaries used consisted of yellow  $(\lambda = .577 \ \mu)$  and blue  $(\lambda = .474 \ \mu)$  as determined by von Kries. The readings are given in Table IV., with the corresponding normal values, and the results are graphically shown in Fig. 6.

TABLE IV.

_λ	Normal Persistence.	Eye Fatigued with $\lambda = .577 \mu$ $\lambda = .474 \mu$ .	λ	Normal Persistence.	Eye Fatigued with $\lambda = .577 \mu$ $\lambda = .474 \mu$ .
.725 µ	.0295 sec.	.0350 sec.	.530 μ	.0138 sec.	.0127 sec.
.710		.0307	.515	.0148	
.698	.0209	.0254	.505	.0155	.0141
.670	.0157	.0166	.495	.0166	
.643	.0135	.0142	.483	.0190	.0182
.615	.0125	.0128	.463	.0251	.0225
.590		.0121	.445	.0334	.0371
.580	.0127		.428	.0398	
.565	,	.0115	.410	.0451	.0491
.554	.0130				

The second pair of complementaries was red ( $\lambda = .656 \,\mu$ ) and green ( $\lambda = .492 \,\mu$ ), determined by Helmholtz. The readings of the

persistence of vision in this case are given in Table V. and plotted in Fig. 7. The normal curve in this figure is the same as that for the preceding case, given in Table IV.

TABLE V.

λ	Eye Fatigued with $\lambda = .656 \mu$ $\lambda = .492 \mu$ .	λ	Eye Fatigued with $\lambda = .656 \mu$ $\lambda = .492 \mu$ .	λ	Eye Fatigued with $\lambda = .656 \mu$ $\lambda = .492 \mu$ .
$.725\mu$	.0353 sec.	.566 u	.0122 sec.	.470 μ	.0204 sec.
.710	.0335	.548	.0125	.463	.0238
.698	.0230	.530	.0130	.454	.0293
.670	.0161	.517	.0137	.445	.0395
.643	.0136	.505	.0151	.428	.0522
.615	.0122	.492	.0167	.410	.0527
.590	.0120	.483	.0182		

On comparing the figures both curves will be seen to be essentially the same, and to differ greatly from the curve shown in Fig. 5. The fatigue curves obtained with the complementary colors are

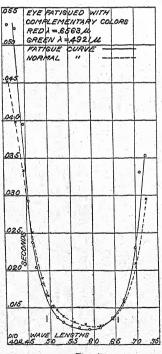
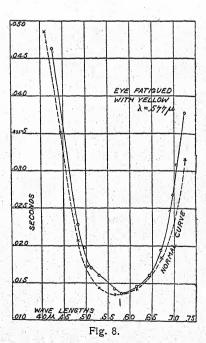


Fig. 7.



elevated above the normal at both ends, which correspond to red and violet, and are depressed below the normal in the middle which corresponds largely to green. The intersections of the curves in each figure (6 and 7) occur in the blue at  $\lambda = .455 \,\mu$ , and in the orange near the yellow, at  $\lambda = .62 \,\mu$ . The effect on the retina of white light of the comparatively few wave-lengths comprised in the complementary colors must of necessity be different from that of the complex mixture of waves forming the white light from an electric arc. The eye is, however, unable to see any difference in the appearance of the two lights when both are of the same intensity; yet measurements of the persistence of vision are capable of showing in a most striking manner the differences in the physiological effects of the two white lights on the retina.

It is most remarkable that the curves in Figs. 6 and 7 are depressed below the normal in the part corresponding to green. For when the eye is fatigued with yellow light ( $\lambda = .577 \, \mu$ ) alone, for example, the resulting persistency curve has two elevations, one in the red and the other in the green, as shown in Fig. 8, which is plotted from the data in Table VI.

TABLE VI.

λ	Normal Persistence.	Eye Fatigued with $\lambda = .577 \mu$ .	λ	Normal Persistence.	Eye Fatigued with $\lambda = .577 \mu$ .
.725 $\mu$	.0315 sec.	.0377 sec.	.566 µ	.0135 sec.	.0142 sec.
.706		.0308	.530	.0144	.0160
.698		.0268	.514	.0156	.0170
.670	.0185	.0194	.497		.0198
.643		.0161	.483	.0206	.0228
.615	.0142	.0146	.445	.0352	
		10 11	.427		.0463
.581	- 1	.0136	.410	.0486	

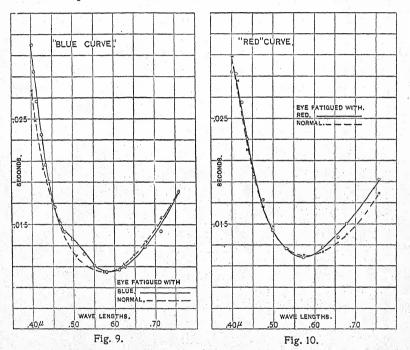
No persistency curve has been obtained when the eye was fatigued with the complementary color, blue, of wave-length .474  $\mu$ . Fig. 9, however, is a persistency curve obtained when the fatiguing stimulus was another blue, the wave-length of which was .440  $\mu$ . This figure is reproduced from the paper previously referred to.

Assuming that the curve for  $\lambda = .474 \,\mu$  would be nearly the same as that for  $\lambda = .440 \,\mu$ , an assumption which is almost certainly

correct, it is seen that fatiguing the eye with blue produces two elevations in the curve, one in the violet and the other in the green. It would seem natural to expect the curve obtained when the eye was acted upon by both colors, wave-lengths .577  $\mu$  and .474  $\mu$ , to have three elevations to correspond with those in Figs. 8 and 9.

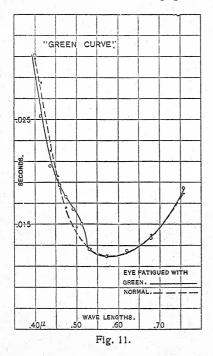
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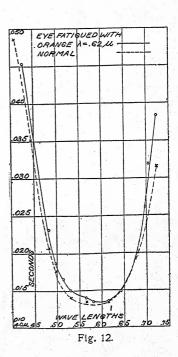
Instead of this, however, the persistency curve in Fig. 6 shows two elevations and one depression. The anticipated *double* elevation in the green is actually replaced by a depression. As the duration of color impressions on the retina is an inverse function of the



luminosity we have the paradoxical conclusion that doubly fatiguing the green sensation with blue and yellow together causes green light to make a more luminous impression than it does normally. Further, since the parts of the curve disturbed by fatiguing the retina with blue and yellow are the red, the green and the violet, it follows that none of the color sensations are independent of each other; while the fact that the curve suffers disturbances in three parts seems to favor the theory of three fundamental color sensations.

The persistency curve in Fig. 7 was obtained, as mentioned before, when the eye was fatigued with red and green of complementary hues. Now when the retina is acted on by red or by green separately a persistency curve is obtained with but one elevation which occurs in the part of the curve corresponding to the color used in fatiguing the eye. This is shown in the curves in Figs. 10 and 11 which are taken from the paper referred to several times.





When, however, the eye is fatigued with complementary red and green colors, the curve (Fig. 7) has an elevation in the red, a depression instead of an elevation in the green, and a pronounced elevation in the violet. It is remarkable that there is no green elevation, and still more remarkable that the violet sensation is affected at all, or at least to any very perceptible amount. It is, perhaps, possible that the white light formed by combining complementary red and green hues is a compound with properties of its own quite different from those of the separate components, and, in virtue of its being white, stimulates all three sensations, red, green and violet, even though no

violet light is present. The same idea would also apply to the curve in Fig. 6, though, as we have seen, the occurrence of the elevations there is susceptible of another explanation.

Both persistency curves obtained when the retina was fatigued by the compounded complementary colors intersect the normal in two places, one in the blue at  $\lambda = .455~\mu$ , and the other in the orange at  $\lambda = .62~\mu$ . This latter color was used as a fatiguing stimulus and a persistency curve obtained which is plotted in Fig. 12 from the data in Table VII. The curve shows two elevations, one in red and the other in green, indicating the generally admitted composite character of the sensation of orange light.

TABLE VII.

λ	Normal Persistence.	Eye Fatigued with $\lambda = .62 \mu$ .	λ	Normal Persistence.	Eye Fatigued with $\lambda = .62 \mu$ .
.725 µ	.0315 sec.	.0383 sec.	.566 μ	.0135 sec.	.0140 sec.
.706		.0319	.530	.0141	.0151
.698		.0261	.514	100	.0166
.670	.0185	.0183	.497	.0177	.0186
.643		.0149	.483	.0207	.0231
.615	.0133	.0136	.427		.0453
.581	1.00	.0135	.410	.0485	

In general we may conclude that the experiments described in this paper strongly support the view that the fundamental color sensations are red, green and violet.

I desire to acknowledge my indebtedness to the kindness of Professor E. L. Nichols, director of the Department of Physics, Cornell University, in whose laboratory these experiments were performed.

University of Manitoba, Winnipeg.

# THE ROTARY POWER OF QUARTZ AT THE TEMPERATURE OF LIQUID AIR.

By F. A. Molby.

THE experiments described in the following communication were undertaken in order to determine the temperature variation in the optical rotary power of quartz, the range studied being that lying between + 20° C. and - 190° C.

The apparatus was very simple and consisted essentially of a Lippich triple field polarimeter, an unsilvered Dewar sphere of about I liter capacity, a small hollow brass cylinder with a compressed fiber strip to suspend it in the Dewar, and a thermal couple with potentiometer for measuring the temperature of the quartz. The brass cylinder had a hole drilled through crosswise for the passage of light and the quartz plate was fixed in the center of the cylinder. The thermo-element was located as nearly as could be at the center of the plate. Cooling was accomplished by filling the Dewar with liquid air to any desired height, up to the line of sight along a diameter of the sphere.

The value obtained by averaging about one hundred settings of the instrument at different times and different days was  $A = 21^{\circ}.214$  per mm. thickness at an average temperature  $-175^{\circ}.2$  C. The same (in the Dewar) gave A = 21.70 per mm. at an average temperature  $19^{\circ}.4$ .

The use of the brass cylinder as a holder for the quartz was for the purpose of securing a uniform temperature over the quartz, since in the vapor from the air a large temperature gradient exists. Measurements at the low temperature were not in close argeement, though all measurements above say — 140° agreed very well. It seemed necessary therefore to devise some better way for obtaining the value at the lower temperatures.

I have constructed a small brass box in which the quartz plate and thermo-element are placed. Two glass tubes with plane glass ends lead into the box; these tubes are provided with side tubes and stop cocks for exhausting the air from them. The box has a lid made in such a way that it can be sealed with vaseline so that when the box is soldered into a thin walled tin can the box may be completely surrounded and covered by liquid air. By this means the box with gaseous air inside is made to take up the temperature of the liquid air, and the quartz plate soon takes up the same temperature as is shown by the thermo-

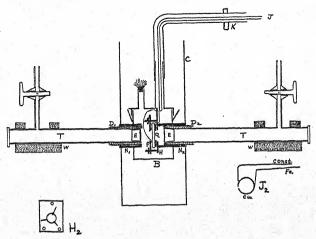


Fig. 1.

junction. By having the tin can heavily wrapped with wool I find that a single filling of liquid air will hold the temperature of the box for approximately an hour with only the small drift which must occur because of the decreasing percentage of nitrogen as evaporation takes place.

The accompanying diagram will show the arrangement of parts and what precautions have been taken to obtain uniformity of temperature and to measure a temperature which is that of the quartz plate.

WW are two wooden supports fitted to hold the tubes in line and to support the whole in the field of the polariscope.

TT glass vacuum tubes 11 mm. in diameter and 11 cm. in length, the inside walls of which are covered with lamp black and shellac.

EE plane glass ends 8 mm. thick, ground into the enlarged ends of TT to make air joints.

 $D_1D_2$  threaded brass tubes about 3 cm. long, with a wrapping of yarn between the brass and the glass tubes TT, and with shellac at the outer ends of  $D_1D_2$ .

 $N_1N_2$  brass nuts into which  $D_1D_2$  are threaded with beeswax and tallow to close the joints.

B is the brass box into which  $N_1$  and  $N_2$  are soldered.

H is a brass plate to hold the quartz. It is soldered to the lid of the box and is held firmly against the lathe-turned end of  $N_2$  by two dove tail lugs of brass, which are soldered to H and slide into slots in the end of  $N_2$ .

Q is the quartz plate in position.

F is a flat fiber plate bolted by three small bolts to the holder H. It is perforated to allow free passage of air.

J shows the leads from thermal junction. They pass through about one foot of rubber tube, which is closed at the outer end by a clamp K.

C tin can for containing the liquid air.

 $J_2$  is a flat view of the junction as it is held against the quartz by the fiber plate F. The two metals of the junction (iron and constantan) are soldered to opposite sides of the copper ring which surrounds the part through which light passes.

 $H_2$  is a flat view of the holder H showing three bits of copper wire soldered on to hold the quartz out from the brass H to admit of air circulation.

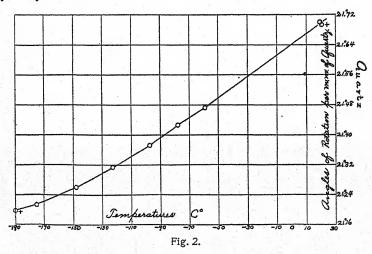
It may be seen that there is no metallic contact of the thermojunction at any point inside the box, and the outgoing wires are wrapped with yarn to separate them from the tube through which they pass. The second brass tube in the top of the lid was designed for an intake to fill the box with hydrogen gas, but in the two sets of measurements made I have allowed air vapor to fill the box, as the metal walls of the box cool before the glass and moisture present will condense there and give no trouble.

The thermo-junction was calibrated with liquid air swimmers, CO<sub>2</sub> snow mixed with ether, ice, and steam, before the copper ring

was inserted. It was also compared with two series junctions both before and after the ring was inserted to show that it registered the same at the — 190° point as it did before the insertion of the ring.

From steam to ice 99°.2 to 0° 
$$E = 538 \times 10^{-5}$$
  
" ice to CO<sub>2</sub> 0° to  $-78^{\circ}$ .2  $E = 388 \times 10^{-5}$   
" "liquid air 0° to  $-190^{\circ}$   $E = 803 \times 10^{-5}$ 

Temperatures were read from a smooth curve drawn through these four points with  $dE/dT = 3.5 \times 10^{-5}$  at  $-190^{\circ}$  as found by the swimmers and by comparison with the series junctions calibrated by analysis of air.



The quartz worked with was 2.86 mm. thick. Fortunately two plates of equal thickness and opposite rotations were at hand. In the work both have been used. The data obtained by the first method are too lengthy for place here but the unstarred points on the accompanying curve give the mean values as obtained by that method. The accompanying data give the observations made by the latter method on June 19 and 20. The starred points on the curve are plotted from these data. On these days the instrument's adjustment was not changed and if we take one half the difference between polariscope readings on L quartz and R quartz we should obtain the average angle of rotation for the two. The zero determinations before and after observations were almost identical on each

Measurements at Liquid Air Temperature.

	$L  \mathrm{Qu}$	artz, June 19, 1	908.		R Qu	artz, June 20	1908.
	R. Ver.	L. Ver.	E×10-5		R. Ver.	L. Ver.	E×10-
			808				804
1	299.80	119.80		1	60°.97	240.97	
			807	2	.87	.88	
2	.75	.75		3	.89	.89	
3	.67	.68	4				803.5
4	.74	.74		4	.83	.83	
			807	5	.75	.75	8
5	.76	.76		6	.94	.94	
6	.70	.70		7	.93	.93	
7	.64	.64					803.5
			806.5	8	.90	.90	
8	.66	.67		9	61.00	241.00	
9	.70	.71		10	.00	.00	
1		1	805	11	60.88	240.88	
10	.64	.64		12	.91	.91	
			804	13	.87	.87	
11	.69	.70		14	.92	.92	
12	.72	.72		15	.89	.90	
13	.71	.71	1	16	61.00	241.00	
14	.71	.70					802
		1. 1. 4.	805	17	60.88	240.89	
15	.78	.78		18	.92	.92	
16	.62	.62		19	.96	.96	
17	.65	.65	1	20	.98	.98	- 3
18	.60	.60		21	.85	.85	
1 * 1			801	22	61.00	241.00	1
19	.66	.67		23	.02	.02	
20	.67	.68		24	60.98	240.98	
21	.62	.62		25	.98	.98	- 1
- 1		1	798		1.0		801
22	.67	.68				-	
23	.62	.62		94 g	- 1		
24	.65	.65					
25	.66	.67	11.0				
			781	1		1 1 1 1	

Aver.  $= 299^{\circ}.685$   $60^{\circ}.926$  Aver.  $T = -190^{\circ}$   $-190^{\circ}$ 

60°.926 — 299°.685 = 121°.241  $a = 60^{\circ}.62$  at  $T = -190^{\circ}$  $a_D$  per mm. = 21°.196 at  $-190^{\circ}$  day; but in each case the readings before do not agree with those made after observations.

Measurements in Box at Room Temperature.

	LQ	uartz, June 20.		R	R Quartz, June 20.				
	R. Ver.	L. Ver.	E× 10-5	R. Ver.	L. Ver.	E×10-5			
13	1		- 107	62.39	242.39				
1	298.31	118.32		.39	.38				
2	.32	.32	1	.37	.37	1			
3	.28	.29	1	.32	.32				
4	.26	.26		.37	.38				
5	.28	.28				-117			
6	.34	.34		.40	.40				
7	.25	.25		.38	.38				
8	.27	.27		.39	.40	25,			
9	.31	.31		.43	.43	-			
10	.35	.35		.35	.35				
11	.27	.27		.35	.35				
12	.29	.29		.37	.38				
13	.29	.30		.40	.40				
14	.33	.33		.39	.40				
15	.30	.30		.39	.39				
16	.28	.28		F 1 5		- 116.			
17	.25	.25	1	.42	.43				
		1	-108	.39	.40				
18	.25	.25	1	.39	.40				
19	.33	.33		.38	.38				
20	.35	.35	- 1	.35	.35	100			

Aver.  $= 298^{\circ}.296$  62°.382 Aver.  $T = 20^{\circ}.0$  21°.6

 $62.382 - 298.296 = 124^{\circ}.086$   $a = 62^{\circ}.043$  at  $T = 20^{\circ}.8$  $a_D$  per mm. = 21°.693 at 20°.8

Approximate thickness of plates is 2.86 mm, by micrometer caliper.

As the readings on low temperatures were made under similar conditions and at the latter part of the day's readings, any errors of the zero should be eliminated by having the two quartzes. Also, as the measurements at room temperature were made on the same day and one directly following the other, the zero reading of the instrument should again be unnecessary. A sodium flame was used and the zero of instrument was read with the tubes, etc., all removed rom the line of sight.

Readings on Zero of Instrument.

	Jur	ne 19.			Jun	e 20.	
Be	fore.	Af	er.	Bei	fore.	Af	ter.
R. Ver.	L. Ver.	R. Ver.	L. Ver.	R. Ver.	L. Ver.	R. Ver.	L. Ver
0.36	180.36	0°.37	180.37	0°.33	180°.33	0.33	180°.34
.27	.27	.52	.52	.32	.32	.38	.38
.25	.25	.52	.52	.27	.27	.44	.45
.35	.35	.44	.45	.32	.33	.34	.34
.31	.32	.47	.48	.28	.28	.38	.38
.36	.36	.41	.41	.32	.32	.39	.40
.27	.27	.28	.28	.37	.37	.40	.40
.35	.35	.42	.42	.30	.31	.45	.45
.26	.27	.38	.38			.43	.43
.33	.33	.37	.37			.40	.41
.34	.35	.35	.35			.35	.35
.36	.36	.29	.30			.40	.40
		.39	.40			.31	.32
		.30	.30		-	.38	.38
		.31	.31	1.0	1.	.38	.38
		.31	.32				
	1 4	.40	.40	-	- ,		
1.0	1	.40	.40		1	. 1	
Aver.	0°.319	Aver.	0°.387	Aver.	0°.315	Aver. (	0°.385

The curve shows a decided tendency to become parallel with the axis of temperatures. It may be noted that Soret and Guye worked several years ago down to temperatures — 71°.5 obtaining a curve of the same form as this one here given. It is hoped that observations may be continued here in the laboratory with liquid hydrogen.

Physical Laboratory, Cornell University, June, 1908.

#### PROCEEDINGS

#### OF THE

### American Physical Society.

MINUTES OF THE FORTY-FOURTH MEETING.

THE society met in the Physical Laboratory of Northwestern University, Evanston, Ill., November 28, 1908, at 10.30 A. M., with Vice-President Crew in the chair. In the absence of the secretary, R. R. Tatnall was appointed secretary pro tem.

The reading of papers was then proceeded with, as follows:

On the Theory of the Carbon Transmitter. BRUCE V. HILL.

Dielectric Losses in Alternating Current Circuits. CARL KINSLEY.

The Hall Effect in Metals at Very Low Temperatures. Alpheus W. Smith.

Magnetic Rotation in Iron Cathode Films. L. R. INGERSOLL.

At 12.45 o'clock, adjourned for luncheon. At 2.30 P. M., the reading of papers was resumed as follows:

The Resistance of Certain Electrolytes in a Magnetic Field. W. W. STIFLER.

A Physical Investigation of Kerosene Oil. G. W. Stewart.

'The Variation of Temperature with Pressure in the Mercury Arc. Chas. T. Knipp.

The Potential Gradient in the Mercury Arc for Different Pressures. Chas. T. Knipp.

A High Temperature Regulator. H. M. RANDALL.

A Method of Determining Thermal Conductivity at High Temperatures. J. K. Clement and W. L. Egy.

The Effect of Mechanical Strains on Thermal and Electrical Conductivity. N. F. Smith.

The Effect of Temperature on the Magnetic Properties of Electrolytic Iron. E. M. Terry.

On the Bursting Strength of Glass Tubing. J. R. ROEBUCK.

A Method of Measuring Alternating Currents. Carl Kinsley and E. J. Moore.

The Charge on the Positive Ion of Ionized Gases. L. Begeman. (Read by R. A. Millikan.)

The Balmer Series for Sodium. R. W. WOOD. (Read by H. Crew.) It was moved and carried that a vote of thanks be extended to Northwestern University for the entertainment accorded the society.

Adjourned about 5.30 P. M.

ROBT. R. TATNALL, Secy. pro tem.

The Distribution of Sound from the Megaphone.1

BY A. G. WEBSTER.

THE sound issuing from a megaphone attached to the writer's standard phone is measured at various angles by the phonometer over both grass and water. With a cone 94 cm. in length and 31.5 cm. diameter and sound of wave-length 134.5 cm. about nine times as much energy is sent along the axis as at right angles, and distinct maxima are found at about fifty degrees from the axis.

THE REFLECTION OF SOUND FROM THE GROUND.1

By A. G. WEBSTER.

WITH the phonometer the sound from the phone is measured at various distances and the interference with the image in the ground is plainly shown, enabling the coefficient of reflection to be determined, and the law of distance to be verified. The reflection is more than ninety-five per cent.

THE DEFINITION OF A PERFECT GAS.1

BY A. G. WEBSTER AND M. A. ROSANOFF.

BESIDES the two gas laws we must have another specification. This may be that the cohesion of the gas is zero, or that the Joule Kelvin cooling is zero. The consequences of both definitions are examined, and the resulting equations of state deduced.

A Physical Investigation of Kerosene Oil.2

BY G. W. STEWART.

THE work was undertaken for the purpose of adding to our present knowledge of the physical properties of kerosene oil and the relations between them. This abstract is the report of the progress made up to the present time. The experimental work was made possible by financial assistance from the State Oil Inspection of North Dakota.

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

<sup>&</sup>lt;sup>2</sup> Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

One of the matters of principal interest in this investigation was "illuminating power." A two-meter bar with standard and secondary standard incandescent lamps, standardized ammeter, and Lummer-Brodhun photometer furnished a satisfactory equipment for measuring candle-power. "Illuminating power" in this abstract means the candle-power-hours-per-gram, the candle-power being measured while using a certain flat-flame oil lamp, arranged always in the same position. Twenty-two different samples of oil were tested. The results are not thought to be of universal application, but for the present must be considered as referring only to oils refined from crudes similar to those of Pennsylvania, Kansas or Ohio. If future experiments show that the results are so limited, they will yet be of service to any investigation of oils from any crude.

The illuminating power of any given sample varies considerably from day to day, and a complete explanation of this variation was not ascertained. Care was taken, however, to use one sample of oil as a standard of comparison, thus reducing all measurements to the same basis.

Measurements were made of the variation of illuminating power with flame height, with different wicks, and with time of burning, and the results obtained were utilized in making any necessary corrections of the data subsequently taken.

Two of the usual tests of illuminating oil are density at 60° F. and residue at 570° F. It was found that the illuminating power had no exact relation with density and residue. Measurements of viscosity also showed no exact relation with illuminating power. In a general way, however, the greater the residue or the greater the viscosity of the oils obtained in the market, the less the illuminating power. Both these measurements can therefore be used as indicators of illuminating power, but occasionally they fail.

It was found, however, that when distillates of one sample are taken, there seems to be a definite relation between density and illuminating power, the latter increasing slowly with the former.

Further, the viscosity of the distillates was found to have a relation with the illuminating power, an increase of viscosity meaning an increase of illuminating power.

These two facts are in apparent contradiction to the statements made above. The explanation rests in the fact that when the distillates of one sample are used they can be regarded as possessing equal refinement; but not so with different samples taken at random in the market.

The presence of detrimental compounds which are not removed in the refining process prevents any definite relation between density and illuminating power, residue and illuminating power, and viscosity and illuminating power, and makes possible this apparent contradiction.

The reason for the decrease of illuminating power in the various samples with increase of residue and viscosity is that these conditions are accompanied by an increase of undesirable compounds.

Whether or not these explanations are true, they led to a discovery which is of considerable interest and which promises usefulness. coefficients of viscosity of samples of oil on the market are compared with what the coefficients should be, judging from the viscosity-density curve of the distillates of a very good sample, then the excess of viscosity is a very good indication of the inferiority of illuminating power. But, further, if what might be called the "normal illuminating power" (or the illuminating power of a very good sample) is multiplied by the ratio of the "ideal" viscosity for that density to the actual viscosity, the result is, on the average, within one per cent. of the actual value found for illuminating power. The maximum difference between computed and observed values is only two per cent. In as much as one per cent. is the limit of accuracy of the experiments, this result is very striking. In making these tests seventeen samples were used, three of them being obtained from independent refineries in Pennsylvania, Ohio and Kansas. This empirical method, then, seems to present the possibility of a simple and easy method of determining the illuminating power if the oils are from these three fields, and this method can be employed with a very small amount of standardized apparatus in a very short time.

The question not yet ascertained is the limit of applicability of the method. If the reason for the operation of the method is correctly given above, then it is quite possible that the viscosity test will materially assist in determining whether or not the detrimental compounds have been properly removed in the refinement of the oil. The measurements of the coefficients of viscosity were made with the capillary tube method, with an accuracy within one per cent. Due regard was paid to temperature variations of density and viscosity. The latter was determined by experiment.

The ability of an oil to maintain a flame of constant height is commonly called the "burning quality." This test is usually made in a straightforward manner, but it is not satisfactory. Preliminary experiments have been performed which show that the burning quality depends quite largely upon the viscosity. (Effects of surface tension did not vary two per cent., while viscosity varied sixty per cent.) Viscosity furnishes a rough indication of burning quality, but future experiments may show that this test, or the combination of it with some other will prove to be a very satisfactory method of determining the burning quality. Residue measurements are also of great importance in this connection.

Undoubtedly some of the work herein noted is not new, c. g., the measurement of viscosity of kerosene oil, but no trace has been found of an investigation similar in character or results.

The detailed publication of the experiments are reserved until a more complete report can be made.

STATE UNIVERSITY AND SCHOOL OF MINES OF NORTH DAKOTA.

THE EFFECT OF TEMPERATURE ON THE MAGNETIC PROPERTIES OF ELECTROLYTIC IRON.<sup>1</sup>

By E. M. TERRY.

THE iron for this work was furnished by Prof. C. F. Burgess, of the Electro-Chemistry Department, and has been shown to have a purity of 99.97 per cent. Rings were cut from the cathode deposit and tested magnetically by a modification of the Rowland Ring Method.

Hysteresis and magnetization curves were taken at temperatures ranging from — 190° C. to 780° C. at intervals of 20° C. to 100° C., both for freshly deposited and annealed samples. The energy loss per cycle and coercive force were found to decrease uniformly with increasing temperature, while the retentivity has a maximum at about room temperature. The permeability for low values of magnetizing force increases with the temperature, reaching a maximum of 9,500 for H=.5,  $T=740^{\circ}$  C. For larger values of H the permeability decreases with increasing temperature.

One sample, after annealing, was found to have a coercive force of only 1.2.

Magnetic Rotation in Iron Cathode Films.1

By L. R. INGERSOLL.

THE writer's bolometric method of measuring magnetic rotations of the plane of polarization for the range of spectrum from about  $\lambda=.6~\mu$  to 2.5  $\mu^2$  has been developed until rotations as small as .001° can be measured under favorable conditions. By this method the rotation on transmission through, and reflection from, thin iron cathode films in a field of about 6,000 units has been measured for various wave-lengths. The two curves obtained in this way, for the Faraday and Kerr effects respectively, are in general quite similar and show an increase of rotation with wave-length to about  $\lambda=1.5~\mu$ . Assuming Kundt's value of 200,000°/cm. as the rotation of iron for yellow light the maximum rotation would be on this basis about 340,000°/cm.

The relation of the reflection rotation to the thickness of the film was also investigated and it was found that a film of less than 20  $\mu\mu$  in thick-

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

<sup>&</sup>lt;sup>2</sup> See Phil. Mag., Jan., 1906, and PHYS. REV., Dec., 1906.

ness contributes more than half of this rotation. Characteristic changes in the curves appear when the films are oxidized, and are accompanied by changes in the absorption or reflecting power of the film.

When the films are overlaid with liquids of various refractive indices the Kerr rotation is found to increase and to be roughly proportional to these indices. On certain assumptions this may be shown to be in accordance with Voigt's theory.

THE HALL EFFECT IN METALS AT VERY LOW TEMPERATURES.1

By Alpheus W. Smith.

THE Hall effect in iron, nickel, cobalt, copper, platinum, cadmium and calcium has been measured at room temperature and at the temperature of liquid air. In the cases of iron, nickel and cobalt curves have been obtained showing the relation between the Hall effect and the strength of the magnetic field. For each of these metals two curves have been plotted, one for  $22^{\circ}$  C., the other for  $-190^{\circ}$  C. The methods of observation were essentially those employed by other experimenters on this effect. The effect in copper, platinum and cadmium increases with decreasing temperature. On the other hand the effect in iron, nickel, cobalt and calcium decreases with decreasing temperature.

PHYSICAL LABORATORY,

University of Wisconsin.

THE EFFECT OF MECHANICAL STRAINS ON THERMAL AND ELEC-TRICAL CONDUCTIVITY. 1

By N. F. SMITH.

A T the meeting of the Physical Society in December, 1907, a preliminary report was given on the changes in the thermal and electrical conductivities of metal bars due to the influence of a stretching force. Since then these measurements have been completed with the following results. In all cases the thermal conductivity of the bars increases when a moderate tension is applied. As the limit of elasticity is approached this increase reaches a maximum. When the tension exceeds this limit the conductivity remains practically constant in the case of steel and brass or begins to diminish in the case of iron and copper. The total change in thermal conductivity due to tension amounts to from 2 to 8 per cent.

The corresponding changes in electrical conductivity are much smaller and in each case the electrical conductivity is diminished under tension.

<sup>1</sup> Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

The same experimental method has been applied to investigate the effects produced by torsion. These measurements are still incomplete but have been carried far enough to show that the thermal conductivity, like the electrical, is diminished by torsion and that the changes in thermal conductivity are much the greater in magnitude.

DIELECTRIC LOSSES IN ALTERNATING CURRENT CIRCUITS.<sup>1</sup>

By CARL KINSLEY.

THE equations showing the distribution of energy in simple alternating current circuits must contain terms giving the copper, eddy current, iron core and dielectric losses. The importance of the iron core loss has been recognized and its amount carefully determined for the conditions usually met in practice. The dielectric loss however although recognized has generally been found to be either negligible or assumed to be so without any actual determination. I have found that frequently the dielectric loss is very large and it may be even larger than all of the other losses in the circuit. The dielectric loss is a function of the temperature and the paper gives determinations for temperatures between — 14° C. and 50° C. Various dielectrics have been examined and whenever they show absorption then the energy losses are considerable.

## On the Theory of the Carbon Transmitter.1

BY BRUCE V. HILL.

A SSUME that, in the transmitter, the diaphragm and carbon granules are perfectly elastic within the limits of vibration imposed upon them by a sound wave. Assume also that the resistance of the granules varies as the pressure through these small limits. If we examine the simple circuit of the local battery instrument and allow a simple sine wave to fall upon the diaphragm, the statement of Ohm's law for this case is

$$L\frac{dI}{dt} - IR\left(1 + a\sin 2\pi nt\right) = E.$$

A complete solution of this equation is

$$I = \frac{E}{L} e^{-\frac{R}{L} \left(t - \frac{a}{\rho} \cos \omega t\right)} \left[ t + \frac{R}{L} \left( \frac{t^2}{2} - \frac{a}{\omega^2} \sin \omega t \right) + \frac{R}{2L^2} \right]$$

$$\times \left( \frac{t^3}{3} - \frac{2at \sin \omega t}{\omega^2} - \frac{2a \cos \omega t}{\omega^3} + \frac{a^2}{2\omega^2} t + \frac{a^2}{4\omega^3} \sin^2 \omega t + \cdots \right) + K.$$

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Evanston meeting of the Physical Society November 28, 1908.

From this equation we see that the current in the primary is equivalent to the direct current I=E/R with an unsymmetrical undulation superposed upon it.

An approximate solution may be obtained by overlooking the inductance of the primary circuit and writing

$$I = \frac{E}{R (1 + a \sin \omega t)}$$

$$I = \frac{E}{R} (1 - a \sin \omega t + a^2 \sin^2 \omega t - a^3 \sin^3 \omega t + \text{etc.})$$

$$dI/dR = -2\pi na \frac{E}{R} (\cos 2\pi nt - a \sin 4\pi nt + 3a^2 \sin^2 2\pi nt \cos 2\pi nt - \text{etc.}).$$

The current in the secondary is then of the form

$$I' = M|Z \cdot dI|dt.$$

This is an alternating current having harmonics present with the fundamental, the octave being the most prominent. Experience with the telephone confirms this result. It is also found that the energy of the fundamental in the voice current is directly proportional to that of the impinging sound wave.

A Method of Determining Thermal Conductivity at High Temperatures.<sup>1</sup>

By J. K. CLEMENT AND W. L. EGY.

THE following method has been devised for the determination of the thermal conductivity of solids at temperatures lying between 400° and 1200° C.

The material to be investigated is made in the form of a cylinder about 12 cm. in diameter and 40 cm. long, with a cylindrical opening through the center large enough to admit an electric heating coil. The cylinder is further provided with several longitudinal openings situated at different distances from the axis and of sufficient size to permit the introduction of a thermo-couple. The temperature gradient perpendicular to the axis is determined by means of a differential platinum, platinum-rhodium thermo-couple. The heat developed is calculated from the number of watts of electrical energy dissipated in the heating coil.

The conductivity K can be computed from the formula

$$K = \frac{0.2394 \, EI}{2\pi^2 l} \times ln \left(\frac{r_2}{r_1}\right) \frac{1}{T_1 - T_2}$$

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

In which "l" is the length of coil, and  $T_1 - T_2$  is the difference in temperature between two points at distances  $r_2$  and  $r_1$ , from the axis.

Some measurements have already been made with soft steel and fire clay. The conductivity of the former falls from 0.2 at 400° to 0.08 at 850° C. That of the latter is nearly constant, about 0.0024, between 450° and 750°. These values are expressed in terms of calories, centimeters, centigrade degrees and seconds.

#### A METHOD OF MEASURING ALTERNATING CURRENTS.1

BY CARL KINSLEY AND E. J. MOORE.

THE following method was devised for the measurement of alternating currents and particularly for the the determination of small variations in the current flowing in a circuit.

A short heating wire of iron, manganin or other material is used to carry the current and about this is wrapped an insulated No. 40 copper wire. The wires are mounted in a glass tube which is exhausted. The short wire carrying the current heats the wire which is wrapped around it and this wire is made of one of the arms of a Wheatstone bridge. Either the galvanometer can be arranged to read the current directly upon a properly divided scale or else a direct current can be sent through the wire of such a value that the heating effect is the same as that due to the alternating current. The direct current can then be read with any of the usual D.C. instruments.

The method has been found to be particularly sensitive and accurate. Some cases in which it has been used were discussed.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

#### THE

# PHYSICAL REVIEW.

#### THE COEFFICIENTS OF GAS VISCOSITY. II.

By WILLARD J. FISHER.

Construction of Apparatus.

THE apparatus described in the following pages was constructed with the facilities and help of the department of physics, Cornell University, and, toward the end of the construction, with the aid of a grant from the Rumford Fund by the American Academy of Sciences, in carrying out a research on the viscosity of gases and its variation with the temperature.

In a previous paper, Part I. of this series, the writer has shown how Sutherland's equation for gas viscosity may be represented by a straight line, and has used the method for finding the two constants of the equation, taking as a basis the published data of von Obermayer, Breitenbach, Schultze, Markowski, E. Wiedemann, Holman and Bestelmeyer. Since the appearance of Part I. Grindley and Gibson have made researches on the flow of air through long metal tubes, and in reducing their results used the same graphical method. All the data published lead to the conclusion that Sutherland's equation accurately represents the facts for temperatures above the critical and pressures such that Boyle's law holds. The graphical representation of the data in Part I. led the writer to look for relations between molecular weight, ratio of specific heats and other constants of pure gases, and their viscosity constants. Certain indications of relations were found, but the

<sup>&</sup>lt;sup>1</sup> Willard J. Fisher, Phys. Rev., 24, p. 385, 1907.

<sup>&</sup>lt;sup>2</sup> J. H. Grindley and A. H. Gibson, Proc. Royal Soc., A, 80, p. 114, 1908.

experimental basis is as yet too narrow for definite conclusions. It is hoped that the apparatus here described will ultimately throw light on this problem, whose solution will undoubtedly bear on that of the partition of energy.

Apparatus — General. — The general idea of the apparatus was suggested by that made at Halle by H. Schultze,¹ and afterward used by H. Markowski, F. Kleint and P. Tänzler. The advantages of Schultze's arrangement are considerable — it has entire symmetry about the capillary and uses but a small quantity of gas, which is forced back and forth through the capillary, and so allows of an indefinite number of determinations with identically the same portion of gas. Hence, also, great pains can be taken to secure purity of the gas used.

In the apparatus to be described all pressures were measured with mercury, and a zero manometer - a barometer, but dipping into the same reservoir of mercury as the manometers for measuring difference of pressure - was made an integral part of the apparatus; this enables the pressures on the two sides of the capillary to be measured with the same steel scale, instead of using two separate scales and a separate barometer. Schultze's water manometer method is no doubt more sensitive, but is also more complicated in construction and use. The gas pipettes and mercury buckets for measuring the volume of gas and securing a constant pressure were all made cylindrical, which allows easier construction and a more nearly automatic method of pressure regulation by an electric windlass; the gas pipettes were calibrated and mounted in such a way that frequent observations of time and volume could be made, to eliminate accidental errors of observation. The capillary was made of Jena 50 III glass, on account of its high melting point and excellent qualities as regards after-working and low expansion coefficient; it was also calibrated by a graphical method, considered to be an improvement on Schultze's, as it permits very numerous observations to be utilized in the calibration. For varying the temperature of the capillary an electric furnace was used, and for measuring its mean temperature a platinum thermometer with compensated leads after Callendar's plan, which plan was also used in the construction of the bridge.

<sup>&</sup>lt;sup>1</sup> H. Schultze, Ann. d. Phys., 5, p. 140, 1901.

Manometers. — The glass parts of the pressure measuring apparatus and connections for filling are shown in Fig. 1, together with the gas pipettes and the water jackets for maintaining a reasonably constant temperature in the pipettes.

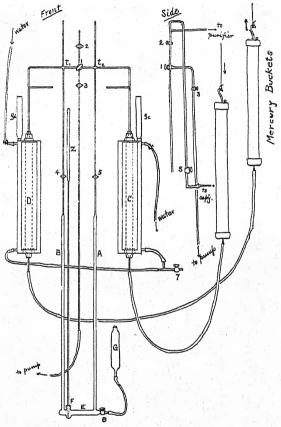


Fig. 1.

A and B are two glass tubes of about 1 cm. bore, 84 cm. long, 12 cm. apart, joined below by a horizontal tube E, 2 cm. diameter, and connected above to two four-way joints  $t_1$  and  $t_2$ . At F there is a cup-shaped opening, and into this there is ground in and cemented tight a tube 94 cm. long; this ends below in a prolongation with a small opening, which dips into a cup formed on the under side of E, and above in a tube Z about 1 cm. bore and 30

cm. length, sealed shut at its upper end. The tubes A and B are the pressure manometers, and by their readings the difference of pressures on the two sides is determined; Z is exhausted of air and inverted in the mercury of E, and serves as a zero manometer; by the difference between its reading and those of A and B the true pressures in the latter are determined. By raising and lowering G the mercury levels in A, B and Z are adjusted.

The four-way joints  $t_1$  and  $t_2$  receive the tubes from A and B before described, and send branches sideways to the gas pipettes through glass springs, upwards to tubes which bend over downward behind the apparatus, join the stopcocks 4 and 5, and then turn backwards to the capillary. Inwards branches go from  $t_1$  and  $t_2$  to a central four-way cock I. From this a branch goes upward through stopcock 2, and bends backward to the gas-generator and purifier; also a branch goes straight backwards from I and bends downward through cock I to the air-pump hose. All tubing not otherwise specified is of about I 5, mm. bore.

With the exception of one well shellacked short rubber connection between cocks t and t, and of ground joints at t and between cocks t, t, and the capillary, all made tight with De Khotinsky cement, the joining of glass tubing was done with the blowpipe, followed by as careful annealing as possible.

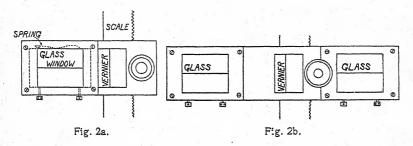
Manometers A and B are not of exactly the same diameter, but fortunately the piece of tube of which the wide part Z of the zero manometer was made was found to give exactly the same capillary depression of mercury as tube B; this was determined by inserting the tube in F, and comparing the levels.

The zero manometer was made with the prolonged lower end closed and bent over at the tip, and was exhausted through the upper end of Z while sealed, in a horizontal position, to a Sprengel pump. During the exhaustion the air film on the walls was removed by heating as hot as it was considered safe to do with a Bunsen burner; then the end of Z was sealed off from the pump, a little nick scratched just above the turned over end of the prolongation, this dipped below the mercury at F, and the tip knocked off. The sealing of the joint with De Khotinsky cement was then completed at leisure.

All stopcocks were made tight with a grease recommended by Prof. A. W. Browne, of the department of chemistry: four parts of vaseline and one of paraffine were melted together, and the mixture filtered hot. This proved very efficient in making tight joints, and has the advantage of being chemically inactive.

The barometer used in checking the zero manometer was by Henry J. Green, of the Fortin type, with brass scale; the internal diameter of the tube is not known, but is estimated to be 1.5 cm.

A portion of the steel scale, with its sliders, is shown in Fig. 2.



It was made by Brown and Sharpe Mfg. Co., and is I inch wide, 3/8 inch thick and 127 cm. long, with graduation to millimeters. is guaranteed accurate at 62° F., which was justified by comparison with a Geneva Society standard meter bar. On its right edge a rack is cut, into which the pinions of the sliders mesh. sliders are of brass; Fig. 2a shows that used with the zero manometer, Fig. 2b one of the two made for the pressure manometers. Either may be moved to any position by a rack and pinion. bearing surface is on the long straight left side of the scale, while strong spring plungers press against the right side to give accurate travel. An opening is out in front to the graduations, and contains a vernier on silver reading to .05 mm. Each slider carries one or two glass windows, with hair lines, adjustable upward by capstanhead screws, pressed against these by springs, and held against the brass frames by felt packing. The hair lines were adjusted in line with the vernier zeros and perpendicular to the bar by the help of the sliding bed and microscopes of a small Geneva Society dividing engine. The vernier zero is placed at the center for convenience in reading the scale. Parallax was eliminated by reflection from

mirrors fastened to the supporting board behind the mercury columns. The hair line was brought *down* to apparent contact with the top of the meniscus. The mercury tubes were tapped before reading, to insure constant form of the meniscus.

The scale was adjusted to the vertical with a reversible level; the vernier readings were checked against each other by measurements of the same height; the parallax mirrors were tested for curvature and inclination with an accurately horizontal telescope provided with a vertical scale and long spirit level - the reflected image of the scale, seen against the cross-hairs, enabled a calculation of the error to be made. The two pressure manometers were also compared, to secure corrections for capillary depression. A table of values was computed for the correction factor to reduce observed heights of mercury to true centimeters at oo C., which covered the range 10° to 30° C., and was applied to all observa-The zero and left-hand manometers, used as a siphon tions. barometer, were compared with the Green barometer, and found to agree with this as well as its somewhat doubtful capillary correction would allow.

Gas Pipettes and Water Jackets. — The original five-foot length of glass tubing from which the pipettes were made was selected from stock, and was very nearly 2.8 cm. in internal diameter at each end and 1.7 mm. wall thickness. The pipettes were about 44 cm. long, and graduated in centimeter divisions with a beam compass, using the same Brown and Sharpe steel scale (marked a) which was used in the calibration of the capillary tube. The graduations were etched in with hydrofluoric acid. The outsides of the pipettes were silvered by Brashear's method, and a strip down the back coated with shellac, then the rest of the silver removed. The graduations were blackened with grease pencil. The construction gives an inverted real image of a graduation-mark, distant from the back two thirds the radius of the tube. By placing the eye in such a position that the tip of a graduation line is in apparent contact with the tip of its image a very efficient correction for parallax is obtained. pipettes were set in the water jackets, cleaned with sodium hydrate. chromic acid and distilled water, stopcocks sealed on below and the upper ends sealed by glass spring tubes to the manometers.

The water jackets were made of sheet copper, each with tubes on the side above and below for admission and exit of water, an opening centrally below for a stopper, with inside a larger circular rim about it for cement; above two openings, one central, with a screw cap (perforated) for a stopper, another beside it, to hold the gauge tube g and thermometer. The pipettes, the glass front windows and the gauge tubes were set with glycerine and litharge cement.

The two water jackets were connected below by rubber tubing, with a T-joint and stopcock 7 for emptying, when necessary. Above, each was connected by a flexible tube to a large water bucket tapped near its bottom. Raising one bucket and lowering the other caused water to flow steadily through the jackets, the rate being controlled by pinch cocks. The glass gauge tubes g showed by their difference of water-level whether water was flowing or not, and also served for the introduction of the thermometers. Since the water supply was thus quite large in quantity, and at the temperature of the room, the temperature of the pipettes could be maintained nearly constant for quite long times.

After setting the parts, allowing the cement to harden, and connecting the pipettes to the manometers, the whole apparatus was exhausted and let stand, to test the tightness of the blown glass joints and the stopcocks. Then the pipettes were filled with mercury and calibrated.

The calibration of the pipettes was carried out according to the following theory.

The volume between the top and any cross-section of a right circular cone is expressed by

$$V = x(a + bx + cx^2),$$

in which x is the distance from the top of the frustum to the section in question, and a, b, c are functions of the base radii and total height of the frustum. Since an ordinary glass tube is somewhat conical, an expression of the same form may express the volume between graduation marks; then x represents the distance between an assumed zero graduation and any other. Volume calibration of a glass tube graduated in centimeters, like one of these pipettes,

consists then in finding the values of a, b, c; these are not to be supposed equal to the coefficients of the right circular frustum, as the elements of the bounding surface are probably not straight lines.

If the length be divided into five parts, whose ends are designated by  $x_0 \cdots x_5$ , then mercury may be run out and weighed and the volume determined from the observed temperature; starting from the point  $x_0$  and running out the portion from  $x_0$  to  $x_1$ , then in addition into the same bottle the portion from  $x_1$  to  $x_2$ , etc., then the masses  $m_1$  (from  $x_0$  to  $x_1$ ),  $m_2$  (from  $x_0$  to  $x_2$ ), etc., are known.  $m_3 - m_0$  is the mass from  $x_3$  to  $x_0$ ,  $m_4 - m_1$  the mass from  $x_4$  to  $x_1$ ,  $m_5 - m_2$  that from  $x_5$  to  $x_2$ ; these masses are nearly equal and determined by independent weighings, while  $x_3 - x_0$ ,  $x_4 - x_1$ ,  $x_5 - x_2$ , are equal if the graduations are good. Call their common value d, and the density of mercury  $\rho$ , constant if the temperature control is good. Then

$$m_0/\rho = x_0(\alpha + bx_0 + cx_0^2),$$
 (1)

and five similar equations with different subscripts. Hence

$$\frac{m_3 - m_0}{\rho(x_3 - x_0)} = \frac{m_3 - m_0}{\rho d} = a + b(x_3 + x_0) + c(d^2 + 3x_3x_0)$$
 (2)

and two like equations with subscripts (4, 1), (5, 2). From these last three equations a, b, c are found.

The equations have been written in the above form for symmetry and hence brevity; but in using them  $x_0$  and  $m_0$  must be taken equal to zero — the calibration must begin with the zero of the graduation. The differences  $x_1 - x_0$ ,  $x_2 - x_1$ , . . , need not be equal; then the computations are slightly longer.

TABLE I.

Pipette.	Mean Temperature.	а	b	e
С	21°.70	5.4750	-0.0005	-1.27.10-5
D	21.38	5.3768	2.47.10-3	3.0 ·10-6

Three sets of weighings were made for pipette D; from them the calibration calculations were carried out, the results forming Table I.

Pipette C was not so accurately calibrated, owing to trouble with the silver coating, and was not often used in runs.

These constants give check values for both pipettes agreeing with the mean weighings much better than the observed weights agree among themselves.

The balance used was a lecture balance by Ruprecht, sensitive to less than .05 gram with over 3 kg. each side. The weights were corrected to .10 gram by standards. Double weighing was used.

For determining the temperature of the pipettes three thermometers were calibrated, Baudin's make, numbers 8,536 (range  $-1.5^{\circ}$  to 30°), 12,979 ( $-2^{\circ}$  to 43°), 15,000 ( $-1^{\circ}$  to 41°), all divided to  $\frac{1}{10}^{\circ}$ . These were tested in melting ice, with the following results, estimating hundredths.

8,536	read	+0.10.	May 15,	1908.	TI	nermometer	dated	Sept., 18	80.
12,979		+ 0.00.	May 11, 1	1906.		44	"	June, 189	91.
		+ 0.00.	Jan. 15, 1	L907.					
"	"	+0.01.	May 30, 3	1908.				,	
15,000	"	+ 0.02.	May 11,	1906.			66	July, 189	9.
6.6	"	+ 0.03.	Jan. 15,	1937.			1		
"	"	+ 0.03.	May 30,	1908.					

The standards for comparison were two sensitive Baudin thermometers, graduated to .02°, which had been calibrated at the Bureau of Standards for the work done by Mr. F. E. Kester in this laboratory on the Joule-Thomson effect. Their ice points were tested by the writer, for comparison with the Bureau of Standards' determinations.

Baudin No.		Bureau Star	V	v. j. f.	
Bauuin No.	Number.	Ice.	Date.	Ice.	Date.
10213	945	0.4206	Mar. 10, 1905	0.420	Dec. 14, 1907
10214	946	0.4600	Mar. 10, 1905	0.460	Dec. 14, 1907

The apparatus for comparison was made of an unsilvered Dewar cylinder large enough to contain all the thermometers to be compared and supplied with a heating coil inside at the bottom, and a tube through which air could be forced to act as a stirrer, which also carried supports for the thermometers. The amount of water used was sufficient for complete immersion of the stems, as this was the way they were to be used in the water jackets. The errors of the three thermometers were determined over a range from 12° to 27°;

and smooth correction curves plotted. The ranges of these corrections were from -.10° to -.15° for B. 15,000; -.05° to -.10° for B. 12,979; -.14° to -.18° for B. 8,536.

This determination of errors is believed to be accurate within  $\frac{1}{40}$ °.

For exhausting the apparatus there was used an oil pump, connected by a short rubber hose and long glass tube to cocks 3 and 1. The vacuum obtained was tested by a small mercury gauge, placed near the purifying apparatus and connected by glass tubing and blown joints to cock 2. The mercury in this gauge was very thoroughly cleaned, and boiled to expel air. Before connecting the mercury buckets and hose, while the lower ends of the pipettes were still closed by stopcocks, the air was pumped out to a 5.5 mm. vacuum and the apparatus let stand for sixteen hours; the whole interior formed one vacuum, the external air being excluded by nine stopcocks. At the end of the time no leakage could be detected by the gauge.

The whole apparatus was supported on a wooden frame, except the electric furnace, which stood on a table screwed to the floor behind the frame. The frame was screwed to the timbers of the ceiling and supported on the floor by small screw-jacks. All parts were fastened together with screws and bolts, and those parts which immediately supported apparatus were made adjustable in two horizontal directions.

Pressure Regulation. — The mercury buckets were made each of a piece of steam pipe, 20 inches long, 1½-inch bore, with screw caps on each end. The upper cap was fitted with a hook and bored on one side of the center with a tapered hole closed with a tapered screw plug. The lower cap was bored for the end of a taper-threaded small iron pipe, for the attachment of the hose for connection to the gas pipettes. After assembling the buckets were cleaned with gasoline, dried, shellacked inside and the joints made tight with shellac; the whole, especially the joints, was then heated hot enough to get rid of the solvent of the shellac. The buckets were suspended from the windlass by the heaviest obtainable tinned braided picture cord.

To test the buckets for tightness, before filling with mercury the

screw plugs were cemented tight, the whole apparatus exhausted to about 6 mm., and let stand. There was a slow leakage shown, due no doubt to passage of air through the rubber tubing or perhaps to escape of air from its walls.

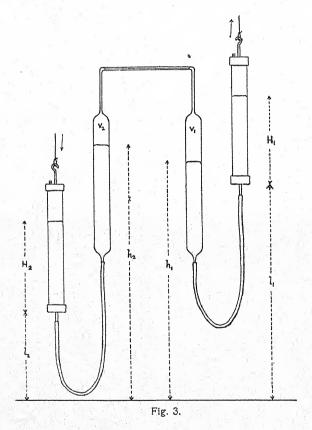
To make sure that this leakage should do no harm by contaminating the pure air or other gas contained in the pipettes, the necessary amount of mercury was put into the buckets and the screw plugs cemented tight. The buckets were laid on the floor, so that all mercury ran down into them, and the whole apparatus exhausted as far as the slow leakage of the pressure tubing and the pump would allow — about 6 mm. The buckets were then raised to allow the mercury to run into the pipettes. Care was thereafter taken to prevent the mercury surface from running down into the hose, so that it was always in contact with glass.

In a similar way, by closing the pinchcock below G, opening  $\delta$  and exhausting, air is removed from the rubber hose which admits mercury to the manometers.

For raising and lowering the buckets an electric windlass was constructed with a  $\frac{1}{16}$  h.p. shunt motor belted to a pulley, giving a speed reduction of  $\frac{1}{2}$ , and two worms and gears in series, giving reductions of  $\frac{1}{61}$  and  $\frac{1}{99}$  respectively; the resulting reduction was then  $\frac{1}{12078}$ . The motor was run separately excited, the field was excited with 110 volts, the armature shunted off a Cutler-Hammer rheostat, with an additional step formed of a tin frame. The range of adjustment was about 100 to 1,200 revolutions per minute. The picture cord was wound up on small iron pulleys of various sizes. The windlass was supported on a wooden pillar resting on small screw-jacks, by means of a wooden frame made exactly adjustable as to height.

All mercury used in the apparatus was cleaned by falling in excessively fine drops a distance of about four feet through a solution of nitric acid and mercurous nitrate, then passing through a gooseneck into concentrated sulphuric acid, then out into a bottle through another goose-neck. This was repeated several times and seems to give very pure mercury; for that used in the vacuum gauge, which had been treated this way more frequently than most of the rest, showed a perfectly flat surface on the vacuum side.

Fig. 3 shows in diagram the essential features of the apparatus for regulating pressure on the two sides of the capillary:  $l_1$  is the height of the bottom of one of the mercury buckets from the floor;  $H_1$  the height of the mercury in this bucket above the bottom;  $h_1$  the height of the mercury level in the corresponding pipette from the floor;  $m_1$ ,  $p_1$  and  $p_2$  the mass, pressure and volume of the gas



inclosed;  $\mathcal{Q}_1$  the cross-section of the cylindrical bucket;  $q_1$  the cross-section of the pipette;  $\rho$  the density of mercury; B the barometric pressure; similarly, with subscript  $_2$  for the other side of the apparatus. The condition for constant pressures on the two sides may be approximately found as follows:

By Boyle's Law,  $p_1v_1=cm_1$ ; since  $p_1$  is constant, any variation will give

$$p_1 \delta v_1 = c \delta m_1$$
.

By the hydrostatic law,  $p_1 + B + \rho g(l_1 + H_1 - h_1) = 0$ ; whence  $\partial l_1 + \partial H_1 - \partial h_1 = 0$ .

Since mercury is not compressible, and pressure tubing does not stretch,

 $Q_1 \delta H_1 + q_1 \delta h_1 = 0.$ 

Since glass tubing is inextensible

$$\delta v_1 + q_1 \delta h_1 = 0.$$

Combining these and a similar set for the other side,

$$\begin{split} & \delta l_1 + \frac{c \delta m_1}{p_1} \left( \frac{\mathbf{I}}{q_1} + \frac{\mathbf{I}}{Q_1} \right) = 0, \\ & \delta l_2 + \frac{c \delta m_2}{p_2} \left( \frac{\mathbf{I}}{q_2} + \frac{\mathbf{I}}{Q_2} \right) = 0. \end{split}$$

In addition there are as connecting conditions, that the mass of gas entering the capillary is the same as that leaving it, whence

$$\delta m_1 + \delta m_2 = 0$$

and that the velocity ratio of the two buckets is constant, owing to the construction of the apparatus, whence

$$\partial l_1 + k \partial l_2 = 0.$$

Reducing these and solving for k,

$$k = \frac{p_2}{p_1} \frac{\frac{I}{q_1} + \frac{I}{Q_1}}{\frac{I}{q_2} + \frac{I}{Q_2}}.$$
 (3)

If  $q_1 = q_2$  and  $Q_1 = Q_2$ , then  $k = p_2/p_1$ . So that by careful selection of the glass for the pipettes and use of cylindrical mercury buckets of the same size, moving with a constant velocity ratio, it is possible to secure constancy of pressure. This condition, expressed in equation (8), is necessary, but not sufficient; for the speed at which the apparatus for raising one bucket and lowering the other must be run depends upon the particular ratio of pressures selected, on the values of those pressures, and on the speed with which the gas under

test passes through the capillary. Trial with air has shown that the condition derived above gives a good clue for starting on trials, and that it is not difficult to find two pressures and a corresponding speed such that the pressures remain constant almost without attention to the motor-rheostat for quite long times.

Computation of the Flow of Gas. — In making runs the instant of passage of the mercury surface by a graduation mark in the pipette was observed for as many consecutive graduations as possible. The time was given by the click of an electrically operated clock, which received an impulse every other second from the Howard standard clock of the laboratory. These observations were computed by subtracting from the volume (reckoned from the zero of the graduation) represented by the last graduation mark observed the volume represented by the first; also the last observed time from the first; this was done again with the next to the last and the second graduation marks and times, and so on for all the observed pairs. The sum of these volume differences divided by the sum of the time differences gives the mean rate of flow of gas In symbols for one pair of observations the constant flow

$$F = \frac{v^{\prime\prime} - v^{\prime}}{t^{\prime\prime} - t^{\prime}}$$

and for any number of pairs

$$F = \frac{\Sigma(v'' - v')}{\Sigma(t'' - t')} = \frac{\Sigma(v'' - v')}{\Sigma(t') - \Sigma(t')}.$$
 (4)

In this  $\Sigma(t')$  represents the sum of the first half of the observed times,  $\Sigma(t')$  the sum of the last half.

Since the volumes to any two graduation marks x'' and x' may be represented by

$$v'' = x''(a + bx'' + cx''^2)$$

and

$$v' = x'(a + bx' + cx'^2);$$

therefore

$$v'' - v' = (x'' - x')[a + b(x'' + x') + c(x''^2 + x''x' + x'^2)],$$

and this relation may be used to shorten the tedious summations indicated above.

The graduations being supposed accurate centimeters, and ob-

servations being taken on consecutive graduation marks, the pairs of graduations first and last, second and next to last, etc., have a common mean, which may be represented by  $x_m$ . For any pair x'', x',

$$x''-x_m=x_m-x'=1,$$

say. Then

$$v'' - v' = 2\Delta [a + 2bx_m + 3cx_m^2 + c\Delta^2].$$

Putting  $a + 2bx_m + 3cx_m^2 = k$ ,

$$v'' - v' = 2 \lceil k \Delta + c \Delta^3 \rceil.$$

For all the observations

$$\Sigma(v''-v')=2k\Sigma A+2c\Sigma A^3.$$

If the number N of observations is odd,  $\Delta$  changes by unit steps from 1 to  $\frac{1}{2}(N-1)$ , and

$$\Sigma(v'' - v') = \frac{1}{4}(N^2 - 1) \left[k + \frac{c}{8}(N^2 - 1)\right]. \tag{5}$$

If N is even,  $\Delta$  changes by unit steps from  $\frac{1}{2}$  to  $\frac{1}{2}(N-1)$ , and

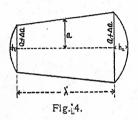
$$\Sigma(v'' - v') = \frac{N^2}{4} \left[ k + \frac{c}{8} (N^2 - 2) \right].$$
 6)

These two formulas enable the computation of a large number of observations to be made with comparative ease.

Capillary Construction and Calibration. — The capillary tube was of Jena 59 III glass, selected by examination of the ends for roundness of the bore and suitable size. A piece of about 50 cm. length was cut, and its ends sealed with the help of a considerable air pressure to short pieces of the same material but internal diameter about 2 mm. and length about 10 or 15 cm. The cleaning in preparation for calibration was carried out with caustic soda or potash, aqua regia, potassium bichromate and sulphuric acid, with water redistilled in glass for washing. The solutions were forced through the tube hot, by inclosing the tube to be cleaned in a glass jacket like a Liebig condenser into which steam was continually passed. The apparatus stood upright, with the lower end of the wide connecting tube passing from the steam bath through a stopper into a side-neck test-tube, where it dipped below the surface of a quantity of the cleaning solution. Air pressure from a reservoir

introduced by the side neck forced the liquid up through the hot capillary. After such cleaning and rinsing with distilled water each end tube was plugged with cotton wool (absorbent cotton) and air from a sulphuric acid drying tube drawn through until no water drops appeared. The tube was examined with a magnifier, and if any discoloration or suspicious spots appeared the cleaning was repeated.

The tube was calibrated by a method suggested by that described



by H. Schultze, 1 but differing from his in the use of a graphical reduction and a larger number of measurements of the mercury thread.

In a good capillary tube an inclosed short mercury thread may be taken to have the form of the frustum of a right

circular cone, capped at each end with a spherical segment of one base (Fig. 4).

Taking a the arithmetical mean radius of the frustum,  $a - \Delta a$  and  $a + \Delta a$  the radii of its two end faces,  $\lambda'$  its height,  $h_1$  and  $h_2$  the heights of its smaller and larger segments, then its volume is given by

$$V = \pi a^{2} \left\{ \left( 1 + \frac{\Delta a^{2}}{3a^{2}} \right) \lambda' - \frac{\Delta a}{a} (h_{1} - h_{2}) + \left( 1 + \frac{\Delta a^{2}}{a^{2}} \right) \frac{h_{1} + h_{2}}{2} + \frac{h_{1}^{3} + h_{2}^{3}}{6a^{2}} \right\}.$$
 (7)

In practice  $\Delta a/a$ ,  $h_1^3$ ,  $h_2^3$  and  $(h_1 - h_2)$  are small in comparison with  $\lambda'$ , and may be neglected, when the formula becomes

$$V = \pi a^2 \lambda' + \frac{\pi a^2}{2} (h_1 + h_2).$$

Assuming the volume of an equivalent cylinder  $V = \pi a^2 \lambda$  we have

$$\lambda = \lambda' + \frac{1}{2}(h_1 + h_2) \tag{8}$$

as its length. This equivalent length of the mercury thread was used in the calibration.

The mean radius a is situated nearly midway between the ends of the mercury thread, with a negligible relative error, practically less than  $\frac{1}{6}\Delta a/a$ .

<sup>1</sup> H. Schultze, Ann. d. Physik, 5, p. 147, 1901.

The calibration is performed in two steps, of which the following is the theory:

I. For Volumes (Fig. 5). — From any arbitrary position (in practice marked by etching the tube) assumed as zero, measure the position l of the center of a short mercury thread, and the length  $\lambda$  of the

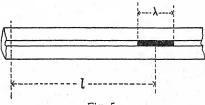


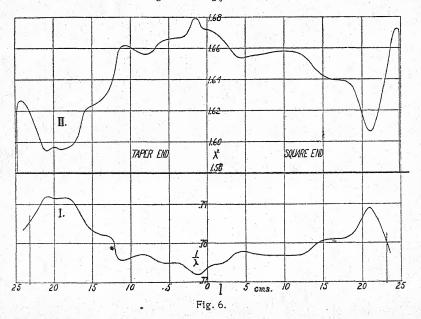
Fig. 5.

thread. At the point l the cross-section of the tube is  $Q = V/\lambda$ , in which V is the volume of the thread. Measured from zero the total volume of the tube to l is v. Also,  $dv = Qdl = V/\lambda \cdot dl$ . If V is kept constant by temperature control,

$$v = V \int_0^1 \frac{dl}{\lambda}.$$

Plotting a curve with  $y = 1/\lambda$ , x = l, (Fig. 6, I.), its area

$$= \int y dx = \int_0^1 \frac{dl}{\lambda} = \frac{v}{V} .$$



The volume V of the short thread cannot be computed accurately by direct weighing, since the container must be of much greater mass than the mercury itself. Hence a more accurate way to find V is to find the total volume of the tube by a long thread between two points l' and l''. Call this volume v'' - v'. Then

$$V = \frac{v'' - v'}{\int_{l'}^{l''} \frac{dl}{\lambda}},\tag{9}$$

in which the integral is the area under the curve already drawn and between the ordinates at l' and l'', so that V is determined in terms of measured quantities.

2. For Viscous Resistance. — The equation for the flow of a gas through a tube of truly cylindrical bore is (omitting the very small correction  $4\zeta/a$ )

$$F = \frac{\pi a^4}{16\rho\eta'l} (p_1^2 - p_2^2) \quad \text{or} \quad \frac{16\rho F \eta'}{\pi} = \frac{a^4}{l} (p_1^2 - p_2^2)$$

(O. E. Meyer, Pogg. Ann., 127, p. 269, 1866; Poynting and Thomson, Properties of Matter, p. 210).

In this F = the volume transpired per second, measured at pressure p;

a = the radius, l = the length of the tube;

 $p_1$  = the entrance,  $p_2$  = the exit pressure.

If this law is assumed true for small lengths, such as the gas may be considered to flow through in series in a tube of slightly varying bore, then for each such tube of radius a and length dl.

$$\frac{16pF\eta'}{\pi} = a^4 \frac{d(p^2)}{dl}.$$

In this the left-hand member is constant. So

$$d(p^2) = \frac{16pF\eta'}{\pi} \frac{dl}{a^4}$$

and

$$\int_0^l d(p^2) = p_1^2 - p_2^2 = \frac{16pF\eta'}{\pi} \int_0^l \frac{dl}{a^4}.$$

Now, from the previous curve,

$$Q = \pi a^2 = \frac{V}{\lambda}; \quad \therefore \frac{1}{a^4} = \frac{\pi^2 \lambda^2}{V^2}; \quad \therefore p_1^2 - p_2^2 = 16pF\eta' \frac{\pi}{V^2} \int_0^1 \lambda^2 dl. \quad (10)$$

Graphical evaluation of  $\int_0^l \lambda^2 dl$ , with the use of the previously de-

termined factor V, gives the calibration factor depending on the shape of the tube. Hence

$$\gamma' = \frac{V^2(p_1^2 - p_2^2)}{16\pi p F \int_0^1 \lambda^2 dl} = \frac{(v'' - v')^2(p_1^2 - p_2^2)}{16\pi p F \int_0^1 \lambda^2 dl \left[\int_v^{l''} \frac{dl}{\lambda}\right]^2}.$$
 II)

(This equation shows that small errors in  $\lambda$  affect the values of the two integral expressions nearly equally but *oppositely*, and so produce an effect on the whole proportional to their difference, and nearly negligible.)

O. E. Meyer shows by discussion of the results of Kundt and Warburg, Warburg and Breitenbach, that  $\zeta$  is numerically equal to the mean free path of the molecule, and like it varies inversely as the pressure. Also, in his approximate solution of the equations of the gas capillary he makes fundamental assumptions which may be shown to lead to the equation

$$\left(\frac{r^2-a^2}{4}-\frac{\zeta a}{2}\right)\frac{\partial p}{\partial x}=\eta u,$$

in which  $\alpha$  is the radius of the tube, r the distance of an element of the fluid from the axis, p the pressure, u the velocity, and x distance parallel to the axis. Assuming  $\zeta = k/p$ , and integrating, the equation for the time rate of discharge is found to be

$$F = \frac{\pi a^{4} (p_{1}^{2} - p_{2}^{2})}{16\eta p l} \left[ 1 + \frac{4}{a} \frac{k}{p_{1} + p_{2}} \right], \tag{12}$$

 $k/\frac{1}{2}(p_1+p_2)$  is  $\zeta$  computed for the arithmetic mean of the entrance and exit pressures.

From the observations  $\eta'$  is computed as above. Using this,  $\zeta$  is computed from the Kinetic Theory equations for mean free path,

<sup>&</sup>lt;sup>1</sup> Kinetic Theory of Gases, R. E. Baynes, Trans., p. 211.

<sup>&</sup>lt;sup>2</sup>O. E. Meyer, Pogg. Ann., 127, p. 268, 1866.

 $\eta' = \frac{1}{3}\rho GL$ ,  $p = \frac{1}{3}\rho G^2$ , with  $p = (p_1 + p_2)/2$ ;  $\alpha$  is the *mean* radius of the tube. Thence the correction term  $4\xi/\alpha$  is applied to give the true viscosity coefficient;

$$\eta = \eta' \left( 1 + \frac{4\zeta}{a} \right). \tag{13}$$

The capillary was marked near its middle with a short scratch etched in with hydrofluoric acid, and this mark used as a reference The tube and a steel centimeter scale were clamped to the sliding plate of the dividing engine, and a pointer fastened to its bed, so that distances moved by the plate and the tube could be read, estimating tenths of millimeters by the scale and pointer. reference mark was brought under the cross hairs, the steel scale read, and the mercury thread brought by air pressure so that one end appeared in the field. The dividing engine screw was turned to bring the edge of the meniscus under the cross, the steel scale and the head of the engine screw were read, the latter to hundredths of a millimeter, and the height of the meniscus was found by two settings with the eyepiece micrometer. This was repeated with the other end of the thread, which was then moved to a new position and the measurements repeated. The thread was forced through the tube several times, and in all 105 measurements of the thread were made.

A Baudin 40° thermometer, No. 12,979, whose bulb was fastened opposite the microscope, was used to find if rapid changes in temperature of the air had any perceptible effect on the length of the mercury thread. On the conclusion being formed that there was no such effect, the thermometer was read only to tenths, and the more gradual changes of the room temperature were observed and corrected for, reducing the thread length to a standard temperature. Calling  $\lambda_2$  the thread length obtained by adding to the length of the frustum the half sum of the two meniscus-heights,  $\lambda_1$  the thread-length at standard temperature,  $t_2$  the room temperature,  $t_1$  the standard temperature,  $\alpha$  the cupical expansion-coefficient of mercury = 0.0001802,  $\beta$  the linear expansion-coefficient of the glass of the tube = .0000059, and neglecting squares and products of small quantities, then

$$\frac{\lambda_1}{\hat{\lambda}_2} = 1 + (\alpha - 2\beta)(t_1 - t_2) = 1 + 0.0001684(t_1 - t_2).$$

The thread of the steel screw of the dividing engine and the graduation of the steel scale (one made by Darling, Brown & Sharpe) were also compared, and found to agree closely enough for the purpose of this experiment on the supposition that the screw was cut at o° C., the scale graduated at 62° F. (which is what the makers advertise). It was found that

$$\frac{\text{scale-readings}}{\text{screw-readings}} = 1.00023.$$

A correction for the temperature at which the measurements were made was calculated and applied, reducing them to the centimeter of the D., B. & S. scale. This scale was compared with a Geneva Society standard meter belonging to the Department of Physics, and was found to be correct.

The measurement of the tube could not be carried out by means of the mercury thread clear to the flaring ends, where the small tube was sealed to the larger heating tubes, so that in these regions recourse was taken to micrometric measurements. The intention was to measure the apparent diameter of the bore of the tube, as seen through the glass, at points whose positions with regard to the zero were also to be measured, and to reduce these to real diameters and equivalent thread-lengths; but the difficulty of obtaining sufficiently concordant micrometer readings was found to be so great that the reduction to thread-lengths was abandoned. Instead, the apparent diameters were measured and from them it was found at what point they became so large that their effect on the resistance factor could safely be neglected. The two points so found were assumed as the ends of the tube. The uncertainty due to this method affects only a few millimeters at each end of the tube, as the flare was very rapid.

Table II. gives the values of l, distance from the reference mark to the middle of the thread, and  $\lambda$ , length of thread, corrected for screw error, temperature and meniscus; the standard temperature assumed was 21°.2 C. The measurements are grouped as made in runs, and the direction from the reference mark is indicated by

TABLE II. CAPILLARY J<sub>3</sub>a.

Run.	I	λ	Run.	I	λ	Run.	I	λ
I.	0.295	1.2930	III.	3.48	1.2910	v.	13.12	1.2859
Taper.	1.165	1.2957	Taper.	4.65	1.2910	Square.	14.84	1.2817
	4.38	1.2902	-	6.405	1.2900		16.87	1.2805
	7.965	1.2867		8.705	1.2885		18.38	1.2801
	9.22	1.2880		9.90	1.2870		19.80	1.2735
	10.625	1.2890		11.295	1.2892		21.15	1.2673
	12.45	1.2796		12.55	1.2793		23.24	1.2830
	13.82	1.2762		14.88	1.2749		23.81	1.2904
	15.645	1.2732		15.085	1.2731		-0.04	1.293
	19.115	1.2631		16.195	1.2734		-0.04	1.293
	20.065	1.2633	-	17.295	1.2667	VI.	-0.03	1.293
	23.22	1.2725		19.60	1.2634	Square.	+0.24	1.291
II.	-0.155	1.2929	,	20.935	1.2628		4.14	1.286
Taper.	+0.375	1.2935		22.33	1.2691		3.21	1.289
	2.285	1.2938		23.595	1.2755	,	1.75	1.291
	3.175	1.2912	IV.	一0.275	1.2923		2.18	1.289
	3.765	1.2907	Taper.	+1.995	1.2945		4.46	1.285
	4.65	1.2915		3.345	1.2909		6.06	1.286
	6.125	1.2900		4.655	1.2904	1	7.36	1.286
	7.39	1.2879	12 12	6.23	1.2900		8.89	1.287
	8.22	1.2870		8.285	1.2868		10.33	1.287
	11.315	1.2894	2 1 1 - 1	11.04	1.2885		10.70	1.287
	12.525	1.2792		12.46	1.2794		13.15	1.285
	13.97	1.2745	-	14.75	1.2749		14.75	1.281
	15.445	1.2733	1.5	15.53	1.2730		16.21	1.280
	16.585	1.2715	1	17.43	1.2646		17.82	1.280
	17.74	1.2639		19.84	1.2635		19.96	1.271
	19.255	1.2631	1	22.005	1.2671		20.92	1.268
	20.51	1.2633		23.58	1.2747		21.96	1.271
	21.605	1.2650	V.	0.14	1.2926		23.57	1.287
	23.105	1.2726	Square.	1.16	1.2920		4.49	1.290
	23.965	1.2756		4.18	1.2863		7.76	1.286
III.	0.325	1.2936		5.98	1.2866		11.61	1.287
Taper.	1.67	1.2958		7.26	1.2870		13.79	1.283
	2.785	1.2917		10.13	1.2874		18.67	1.278

the forms of the flaring joints at the two ends, one widening very rapidly, called *square*, the other more slowly, called *taper*.

Fig. 6 gives the complete calibration curves, reduced in scale too much to show the plotted points.

The tube was filled with mercury within the limits to which the above calibration had been extended, and the position of its ends

with regard to the reference mark was measured with the Brown & Sharpe centimeter scale and sliders (with glass windows, reference lines and mirrors) made for use with the manometers of the pressure-measuring apparatus. This thread was then forced out into a light blown glass container, and weighed with a Troemner Assay balance (sensitive to about 0.06 mg. per scale division deflection with the load used) and a set of quartz and platinum weights, No. 972, whose corrections were known by a certificate of the Normal Aichungs-Commission, dated February 18, 1898. The method of double weighing by vibrations was used, with proper precautions about dryness, handling, etc., and corrections were made for air-buoyancy. The mercury used in both long and short threads was previously cleaned a long time with mercurous sulphate and sulphuric acid; and the particular globule which composed the long thread has kept its surface untarnished after many months.

Computing was done with slide-rule or five-place logarithms, according to the degree of accuracy required. Small tables were constructed for computing the temperature corrections. Marek's values of the specific volume of mercury were used, as found in the "Smithsonian Tables." Weddle's method was used in computing the area of curves. All computations were carefully checked by repetition.

Table III. gives the data on the long thread, the lengths being each the mean of three measurements agreeing within .05 mm.

# TABLE III. CAPILLARY /3a.

Temperature,	21.24° C.
Reference mark to end next taper seal,	23.195 cm.
" " " square "	23.153 cm.
Total length,	46.348 cm.
Error in length (estimated) .05 mm.,	.01 per cent.
Mass,	56.96 mg.
Error in mass (estimated) $< \frac{1}{30}$ mg.,	<.05 per cent.
Volume,	.004209 c.c.
Error of volume (same as error of mass),	<.05 per cent.

The area of curve I, between the ordinates corresponding to the ends of the long thread, was found to be 36.1558 cm<sup>2</sup>. By the method of calibration, the volume V of the short thread was found

to be 0.00011373 cm<sup>3</sup>. The area of curve *II*, for the whole tube, was found to be 75.5127 cm<sup>2</sup>. Hence, substituting in the calibration formula (11), the calibration factor

$$\frac{(v''-v')^2}{16\pi \int_0^l \lambda^2 dl \left[\int_{l'}^{l''} \frac{dl}{\lambda}\right]^2}$$

is found to equal  $3.5703 \cdot 10^{-12}$  at  $21.2^{\circ}$  C., with an estimated error of .05 per cent. To correct for expansion of the glass at  $t^{\circ}$ , multiply by  $[1 + 0.0000174 (t - 21^{\circ}.2)]$ .

A uniform tube 49.6 cm. long and 0.1096 mm. in diameter would be equivalent to this one.

The average value of the meniscus height was found to be  $h_1 = 0.0026$  cm.,  $h_2 = 0.0021$  cm.

Hence the error of neglecting  $(h_1^3 + h_2^3)/6a^2$  is about .01 per cent. of the average thread length; also, from curve I for volumes, (at the point marked \*) it may be shown that  $\Delta a/a$  is never greater than .00191, which justifies the neglect of both in comparison with the other terms of the formula for thread volumes (7).

After calibration the two end tubes were sealed to long pieces of the same glass, and these were bent parallel to the capillary; one also was bent back about 25 cm. from the end of the capillary, so that these connecting tubes projected side by side at the one end of the capillary, but were of nearly equal lengths. As Jena 59 III seems not to seal to soda glass such as the pressure measuring apparatus was made of, the connecting tubes of both Jena and soda glass were joined by ground joints made tight with De Khotinsky cement. This construction gave a strong air-tight joint between the two sorts of glass, and was convenient when it became necessary to take down the apparatus for reconstruction of some of its parts. The two U-shaped bends insured that all gas entering the capillary should have first been warmed to the temperature of the space surrounding the capillary and thermometer.

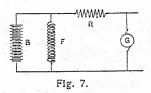
Electric Furnace.— The electric furnace used was made by the Cambridge Scientific Instrument Co., a platinum foil spiral on a

<sup>&</sup>lt;sup>1</sup> Out of 105 measurements of meniscus heights, front and rear, the front meniscus was higher than the rear in only six cases.

porcelain tube about 61.5 cm. long and 4 cm. internal diameter, heat insulated with air space and asbestos paper sheathing; its resistance at room temperature was about 0.63 ohm; at 350°, about 1.26 ohms. It was rated to stand 110 volts and 33 amperes.

The power connections are shown in Fig. 7. G is a motor-generator set, giving very accurate regulation with either 55 or 110 volts at its terminals, and within 1 per cent. or 2 per cent., in spite of various heavy drafts upon the current, at the furnace terminals. Owing to the nearness of the heating coil to the inner air-bath space these variations made it necessary to have some steadying source, which was done by connecting a storage battery B of 10 large cells across the terminals of the furnace F. These cells could be arranged in any convenient combination for varying the resistance and E.M.F., and tin frames R in series with the generator regulated the main current till the potential difference at the furnace terminals on the average just balanced the E.M.F. of the particular combination of cells used. This steadied the furnace current considerably.

The furnace was started warming some hours before a test with a current considerably larger than that needed to produce a desired temperature; when the thermometer showed that this temperature had been passed, the current was



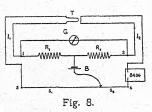
cut down and the potentials adjusted to the battery E.M.F., and the temperature allowed to settle to a steady value. As this was a very slow process toward the end, and the temperature would keep rising for a very long time, the final adjustments were made by slight variations in the resistance R.

Both the thermometer tubes and the prewarming tubes for the capillary were cemented to the openings of the furnace by building about them in place plugs of asbestos stove lining; this becomes quite hard on drying, and is very resistant to the action of heat.

Platinum Thermometer and Bridge. — The temperature of the interior of the furnace, and so presumably of the gas flowing through the capillary, was measured with a resistance thermometer and Wheatstone bridge of Callendar's pattern. The galvanometer used was a Rowland D'Arsonval, read with telescope and scale, and

sensitive enough to indicate  $\frac{1}{5000}$  ohm at the higest temperature observed. The resistance of the galvanometer was about 500 ohms.

Fig. 8 shows the connections. B is the dry cell, G the galvanometer,  $R_1$ ,  $R_2$  are two equal ratio coils, of No. 28 manganin wire, 0.34 mm. diameter, twisted to avoid self-induction, and shellaced; resistance about 26 ohms, and adjustment to equality within .004 per cent., by the Cary Foster method. They have been frequently tested for equality by reversal, and show no change. T is the thermometer,  $l_1$  its leads,  $l_2$  the compensating leads; these leads were made of twisted lampcord, equivalent to No. 12 copper wire, about 400 cm. long, carefully cut to equality in length, and when tested by interchanging on this bridge showing no difference greater than .0001 ohm.  $S_1$ ,  $S_2$  are the segments of the slide wire, of manganin, 50 cm. long, 1 mm. diameter stretched over a half meter stick graduated in millimeters; the key had a contact of manganin off the same spool as the slide wire, and its index error was determined. The slide wire was calibrated in steps by the Cary Foster method, comparing it with a standard . I ohm coil, Hartmann & Braun No. 2115, and found to be accurately uniform within the limits of error, and to have a resistance of I ohm for 184.61 The resistance box No. 8406 was by Leeds & Northrup, three decades, tenths, units and tens, manganin wire on wooden spools; it was guaranteed to . I per cent. and found to be better; the error of every coil was determined to .001 ohm by the Cary



Foster method, comparing the tenths decade with the above Hartmann & Braun .1 ohm coil, the units decade with O. Wolff I ohm coil No. 3403, the tens decade with O. Wolff 10 ohm coil No. 3204. I, 2, 3, 4 are mercury cups, allowing of the easy reversal of the ratio

coils or slide wire. With the exception of these cups and the box, battery and galvanometer binding posts all connections were soldered. The wires joining the various parts of the bridge were copper, 2.09 mm. diameter, carefully cut to equality in length.

The bridge was finally tested by measuring with it the following

standard coils, and also the platinum thermometer wire calibrated by the Bureau of Standards, with the following results:

#### TABLE IV.

Hartmann & Braun,	.1	ohm,	No.	622,	measured	0.1006	hms.
O. Wolff,	1	ohm,	"	3403,	"	1.000	4 4
Hartmann & Braun,	10	ohms,	66	675,	4.4	10.000-	"
O. Wolff,	10	ohms,		3284,	4.6	10.000+	"
Hartmann & Braun,	100	ohms,	"	630,	44	100.008	66
Platinum wire in ice					44	5.901-	"
Platinum wire in ice	after	heating	to 5	70°		5.888-	"

In use the following formula is applied, adding algebraically to the corrected box resistance R = 0.1083x - 0.2679, x being the scale reading, uncorrected. The formula contains all corrections. Slight variations are observed, due, no doubt, to varying plug resistances. These may amount, judging from trials at different times, to .0003 ohm, which cannot affect the measurement of temperature by more than  $\frac{1}{80}$ ° C. Resistances measured with this bridge may be considered certain within .002 ohm.

On account of the length of the capillary it was necessary to use a means of finding the average temperature along it; as the gas was inclosed in glass walls it was decided to have the resistance wire also in a glass envelope, so as to have similar conditions.

This platinum thermometer was made of No. 35 wire procured from the Leeds and Northrup Co., of Philadelphia, as specially refined for the construction of such thermometers. A piece about 86 cm. long was fused at each end to heavy silver leads about 50 cm. long, 1.035 mm. diameter cut carefully to equality in length, and a current was passed through sufficient to raise the platinum to a white heat for several minutes. The platinum and leads were then inserted in a tube of Jena 50 III glass, which was bent at the middle into a U-shape. Another piece of silver wire, cut to a length equal to the leads, was inserted into a short tube of the same glass and the whole bent into a smaller U. The leads were secured in the tubes (during the test at the Bureau of Standards) with dental cement, later the ends of the tubes with the leads were cast in a plug of litharge and glycerine cement. Both tubes were placed in a mold of proper shape, and a stopper-shaped plug of asbestos stove-lining cast about them so that about 14 cm. of each silver lead-wire, both actual and "dummy," would be within the furnace or temperature-bath. After drying thoroughly the apparatus was sent to the Bureau of Standards, at Washington, where it was tested according to the "S.B.P." method of Callendar and Griffiths.

Unfortunately it turned out that the annealing of the wire before this calibration was insufficient, so that after a test at about 570° the resistance in ice had changed .012 ohm. The constants for steam and ice were therefore redetermined, giving the following measurements.

Before	heating	to 570°.			
1. June 19, 1	.908, re	sistance in ice,	5.901	mean of	2.
After h	eating t	o 570°.			
2. June 22, 1	esistano	ce in ice,	5.888	mean of	4.
3. June 24,	4.6	steam at 99°.15,	8.148	**	4.
4. July 11,	66	in ice,	5.887		4.
5. Aug. 1,		in ice,	5.886	46	6.
6. Aug. 1,		steam at 99°.20,	8.148	"	5.

From the observations of the Bureau of Standards, September 17, 1907.

$$R_{\rm o} = 5.8985, \ R_{\rm 100} - R_{\rm o} = 2.2802, \ \hat{o} = 1.50.$$

From the writer's measurements, after heating to 570°,

 $R_{\rm 0}=$  5.888,  $R_{\rm 100}-R_{\rm 0}=$  2.279,  $\delta=$  1.50 (assumed unchanged from the above).

The observations on air were mostly computed with these constants.

After further heatings above 500°,

$$R_0 = 5.886, R_{100} - R_0 = 2.280, \delta = 1.50.$$

The observations on  $N_2O$  were mostly computed with these. In the above  $\delta$  is the correction constant in Callendar's equation

$$t = \frac{R_t - R_0}{R_{100} - R_0} + \delta \cdot \frac{t}{100} \cdot \left(\frac{t}{100} - 1\right).$$

The unusual method of connection, with the galvanometer in circuit all the time, the battery connected by a key to the slidewire, is justifiable only in case self-induction is negligible. That this was so was determined by inserting in place of the platinum

thermometer wire a similar loop of copper wire, of too low resistance to be warmed by the measuring current, and finding that all evidences of self-induction were absent, it was concluded that a small "kick" given by the galvanometer on pressing the battery key, and which was always in the same direction, but only evident when the bridge was nearly in balance, must be due to this cause: the platinum is warmed by the measuring current, and so when the battery key is first pressed the resistance is lower than it is a little later. Hence the galvanometer first throws slightly in the direction indicating low resistance, then rapidly drifts the opposite way. This behavior was invariable, the directions being reversed on reversing the battery.

The arrangement is very convenient, once it is shown by test to be allowable, as the thermal E.M.F.s of the system produce a constant deflection which serves as a zero. The balance was assumed to be found when, on pressing the battery key, no perceptible kick was observed, but after hesitating a second or two the galvanometer would drift toward the high temperature direction. At the definite and constant temperatures of steam or melting ice results were thus obtained consistent to within the limits of the bridge calibration.

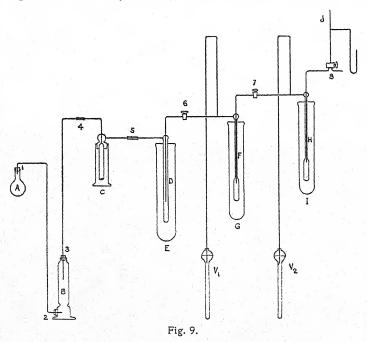
Method of Filling with Air or Gas. — To fill the apparatus with air or gas, open  $\delta$  and lower G to give free connection between B and A. Turn I to connect  $t_1$  to pump through  $\mathfrak{Z}$ , and at the same time  $t_2$  through  $\mathfrak{Z}$  to the purifier. Lower the buckets to empty the pipettes. Close  $\delta$ . Exhaust to as high a vacuum as the pump will give; 0.55 cm. was found attainable with five minutes pumping. Admit the air or gas by opening the cock of the purifier. Exhaust and fill twice more to wash out impurities. Close  $\mathfrak{Z}$ ; set I across, to put  $t_1$  and  $t_2$  in communication. Raise buckets, giving excess internal pressure, which may be reduced by opening  $\mathfrak{Z}$  and pumping out. Open  $\delta$ , and raise G, so that the mercury stands in A and B at the desired level; close  $\delta$ .

## III. PRELIMINARY TESTS ON AIR AND NITROUS OXIDE.

Purification of Air. — The apparatus for purifying air consisted of three Drechsel washing flasks and two stopperless blown glass calcium chloride tubes, with stopcocks on each side of the calcium

chloride tubes. The ground stoppers of the Drechsel flasks were tightened, the first with stopcock grease, the second and third with shellac. The second and third Drechsel flasks and the calcium chloride tubes were connected with blown joints. The first two Drechsel flasks contained a strong solution of sodium hydrate, the third concentrated sulphuric acid. Air was allowed to bubble slowly through the series of reagents, until the flow ceased. It was assumed that removal of water vapor and carbon dioxide was complete without further tests.

Preparation and Purification of Nitrous Oxide. - Fig. 9 shows the



apparatus constructed for this purpose. The general plan of the method is that of Moissan, with slight modifications to increase its safety and convenience.

A is the generating tube, containing commercial ammonium nitrate (Merck's), B is a drying jar, containing calcium chloride, C a Drechsel bottle, with concentrated sulphuric acid. D, F and H are congealing tubes through which the gas must pass in tandem; they

<sup>&</sup>lt;sup>1</sup> H. Moissan, Comptes Rendus, 137, p. 363.

are surrounded by Dewar flasks E, G and I, which can be set at any desired heights or removed from the congealing tubes altogether. E contains a paste of carbon dioxide snow and alcohol, G and I contain liquid air. I is a rubber stopper, tied down, 2 a rubber and 3 a cork stopper, both well shellacked, 4 and 5 are rubber connections; beyond these there are only glass stopcocks 6, 7 and 8 and solid blown glass connections, clear to the the air pump and viscosity apparatus. Between 6 and F and between 7 and F rise up T-tubes which bend over and descend with vertical ends over a meter long, dipping below into a mercury valve tubes  $V_1$  and  $V_2$ . These are adjustable for height, so that sufficient internal pressure may be secured up to 25 cm., and they allow of complete exhaustion with no danger of leakage. F is the lead tube connecting with the air pump and experimental apparatus.

Gentle warming of the ammonium nitrate in A melts it and sends off a slow current of mixed nitrous oxide and water vapor. The valves are set so that gas passes out at  $V_2$  more easily than at  $V_1$ . Water vapor is removed in B, C and D, and the nitrous oxide is frozen in F. Cock  $\delta$  is then closed, 7 and  $\delta$  are opened, and the apparatus is exhausted. By lowering G to a proper point the nitrous oxide gradually sublimes over into I, where it is again frozen. Cock T is then closed, and the exhaustion repeated, after which lowering I allows the I0 to sublime over and fill the viscosity apparatus. As the pressure rises the solid I10 suddenly melts; when the pressure is sufficiently high it passes off through the valve I20.

In this preliminary work no analysis of the air or gas used was made, time and facilities both being lacking. In future work this will not be neglected; though it should be remarked that Moissan, in his note on the method, says that with a proper choice of refrigerants all perceptible impurities were removed from his samples, and this with little reference to the method of generation, which might be such as to give very impure products.

Summaries of Results on Air and Nitrous Oxide. — The two following tables give values obtained in trial runs with air and nitrous oxide. While the work was carefully done, and extends to temperatures 200° higher than any which have ever before been attempted with glass capillaries, or indeed with any calibrated capillaries,

it is to be regarded as only preliminary for several reasons. The most important of these is the regulation of the temperature of the pipettes, which is not yet sufficiently under control to insure without fail an accuracy of much better than a half per cent. Even at high temperatures the temperature of the furnace generally was under sufficiently good control to give an accuracy of one tenth per cent.

TABLE V. Viscosity of Air.

Run No.	Temp. °C.	η - 104	θ	$\frac{\theta^{\frac{3}{2}}}{\eta} \cdot xo^{-7}$
1	24.8	1.845	297.8	2.788
2	24.0	1.835	297.0	2.790
3	481.7	3.519	754.7	5.890
4	479.3	3.222	752.3	6.415
5	22.6	1.848	300.0	2.814
6	23.7	1.845	296.7	2.774
7	347.0	3.008	620.0	5.13
8	25.3	1.915	298.3	2.920
9	25.7	1.829	298.7	2.825
10	489.4	3.562	762.4	5.915
11	496.9	3.607	769.9	5.83
12	498.0	3.551	771.0	6.03
13	501.2	3.606	774.2	5.97
14	23.0	1.849	296.0	2.755
15	220.2	2.735	493.2	4.01

Table V. contains the results on air, which are also graphically displayed in Fig. 10, curve I. The points on this curve have standing by them numbers indicating how many runs are averaged to get the coordinates of the points.

TABLE VI. Viscosity of N<sub>2</sub>O.

Run No.	Temp. °C.	η - 104	θ	$\frac{\theta^{\frac{3}{2}}}{\eta}$ o <sup>-7</sup>
1	26.2	1.517	299.2	3.606
2	75.8	1.739	348.8	3.746
3	141.6	1.970	414.6	4.285
4	183.1	2.161	456.1	4.51
5	25.0	1.498	298.0	3.438
6	224.4	2.348	497.4	4.73
7	289.9	2.610	562.9	5.12
8	413.6	3.073	686.6	5.86

Table VI. contains the results on nitrous oxide, and curve II of Fig. 10 shows the same. In the plotting of the points of this curve the points marked with a ring are those of the present research, those with a cross are von Obermayer's. Points at or below the critical temperature are neglected.

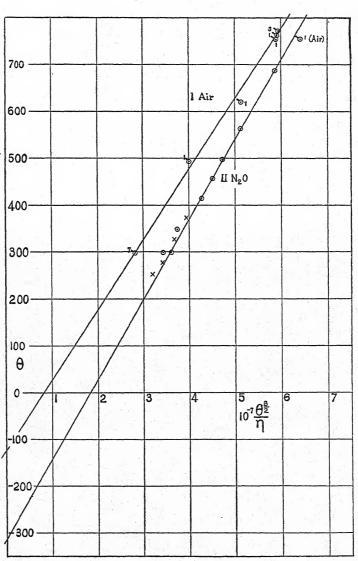


Fig. 10.

In computing these data the values of temperature and viscosity have been found using five-place logarithms; those of  $\theta^3/\eta$  with a slide-rule. The values of  $\eta$  are not corrected for slip. The curves are drawn by estimation.

From the curves we derive the following constants:

Air 
$$C = 124$$
  $K = 150.2 \cdot 10^{-7}$  W. J. F.  
 $N_2O$   $C = 314$   $K = 170.7 \cdot 10^{-7}$  W. J. F.  
 $= 312$   $= 173.8 \cdot 10^{-7}$  von Obermayer.

It is hoped to continue the work with certain improvements in the apparatus and greater accuracy in the corrections, and to determine viscosity coefficients for all the gases to which the apparatus is adapted.

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1 See Part I., p. 393.

# THE EFFECT OF TENSION ON THERMAL AND ELECTRICAL CONDUCTIVITY.

By N. F. SMITH.

HE development of the electron theory of metallic conduction has given new interest to measurements of thermal and electrical conductivity. Since it has been shown that the ratio of the two conductivities is approximately constant for all metals it is natural to expect that anything which produces a change in the one would cause a corresponding change in the other. The effect of tension on the electrical conductivity of wires has been measured by Cantone, Williams, 1 Ercolini, 2 Gray 3 and others. These measurements have been made on small wires stretched by correspondingly small weights. It has been shown that, in general, the resistance of such wires increases when under tension; that up to the elastic limit, the increase in resistance is nearly proportional to the stretching force; that beyond this state, the change is roughly proportional to the elongation. Bismuth shows a change in the opposite direction. So far as the writer knows, no measurements have been made upon the corresponding thermal problem. In 1888 F. Kohlrausch 4 compared the thermal and electrical conductivities of various specimens of steel when tempered to different degrees of hardness. He found that while the conductivities changed by as much as 50 per cent.. their ratio remained practically unchanged.

The present investigation was undertaken to determine what changes, if any, are produced in the thermal conductivity of metal bars when they are subjected to a stretching force, and to compare these changes with those which are produced in their electrical conductivity. Two distinct problems were therefore presented, the one involving thermal measurements, the other, electrical. In neither

<sup>&</sup>lt;sup>1</sup> W. Ellis Williams, Phil. Mag., 13, p. 635, 1907.

<sup>&</sup>lt;sup>2</sup>G. Ercolini, N. Cimento, 14, p. 537, 1907.

<sup>&</sup>lt;sup>3</sup> T. Gray, Trans. Roy. Soc. Edin., 1880.

<sup>&</sup>lt;sup>4</sup> F. Kohlrausch, Wied. Ann., 33, p. 678, 1888.

case was any attempt made to determine the absolute value of the conductivity, but merely the per cent. of change produced by the stretching force.

### THE METHOD.

The method adopted for the thermal problem was substantially that of Wiedemann and Franz. Two bars A and B, of the same size and material and as nearly alike as possible in every respect, were heated at one end to a constant temperature. When the steady state was reached, a point was determined on B whose temperature was the same as that of a fixed point on A. B was then subjected to a stretching force while the condition of A remained unchanged. When the steady state was again reached, a new point was determined on B having the same temperature as the fixed point on A. Assuming that the conductivity is proportional to the square of the length from the hot end to this point of constant temperature, we have a means of measuring the change produced by the force applied. While this assumption is not rigorously true, yet, since the changes in conductivity are relatively small, the error introduced by its adoption is less than the experimental errors.

It seemed desirable to study the changes in the electrical conductivity of the same bars used in the thermal problem and under the same conditions. Accordingly the electrical resistance of a measured length of the bar B was compared with that of approximately the same length of bar A as each successive tension was applied to B. The method here used was a modification of the Kelvin "double-bridge method" due to J. H. Reeves.

### THE APPARATUS.

After many modifications the apparatus finally used was constructed as shown in plan in Fig. 1, and in elevation in Fig. 2. Round bars were employed  $\frac{5}{16}$  inch in diameter and about  $4\frac{1}{2}$  feet long. The bars A and B were mounted horizontally side by side about 3 inches apart. At the left-hand end they passed completely through a cast-iron box C, each edge of which was 8 inches and whose sides were 1 inch thick. This rested on a tripod stand over a Bunsen burner. The box was provided with a cast-iron lid and was thickly wrapped in asbestos. On the inside of the box the bars

were clamped between two heavy pieces of copper D, one above the other, each 5 inches long,  $1\frac{1}{2}$  inches wide and 1 inch thick. These were bored out to receive the bars and held together by bolts. The bars were carefully insulated from the box and from the copper clutch by thin sheets of mica. A hole in the center of the copper

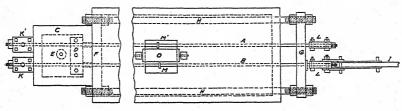


Fig. 1.

clutch received the bulb of a thermometer whose stem projected through the cover of the box. The copper clutch was maintained at a constant temperature by a thermostat. This consisted of a mercury bulb E, placed at the bottom of the box directly over the flame, having a capillary stem projecting above the cover. A wire inserted in the top of the stem touched the mercury when a certain

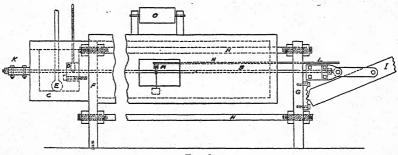


Fig. 2.

temperature was reached. This closed an electric circuit and shut off the gas from the burner. As soon as the temperature commenced to fall the circuit was opened and the gas turned on and lighted by a small pilot light which burned continuously. Some difficulty was experienced in making the mercury bulb respond quickly enough to the changes of temperature. It was at first submerged in a bath of paraffin, but this was given up because of the

smoke given off when somewhat high temperatures were employed. A bath of mercury was next used, but this partly vaporized and then condensed in the cooler parts of the box, destroying the insulation of the bars. Finally, the alloy used in making fuse wire was employed. This melted at the temperatures used, but did not vaporize and secured intimate thermal connection between the bulb and the bottom of the iron box. With this arrangement the thermometer, graduated to degrees, showed no measurable variation. If there was a slight variation in the temperature of the copper clutch it affected both bars alike and hence introduced at most a very slight error in the results.

In order to apply tensions equal to the breaking strength of the bars it was necessary that they be mounted in an extremely rigid frame. This was constructed as follows: A cast-iron plate F, 11 inches wide,  $1\frac{3}{4}$  inches thick and 13 inches high, was mounted upright on a table immediately in front of the iron box. A similar plate G was mounted parallel to the first and about 36 inches in front of it. The bars under observation passed through suitable holes in these plates, being insulated from them by fiber tubing. Four  $\frac{3}{4}$ -inch iron rods H, connected the two plates, and double nuts at each end of each rod held the plates securely in position. Two  $\frac{3}{8}$ -inch iron rods were screwed into the bottom of the plate F and made fast to the floor joists below. Two other rods  $\frac{1}{2}$  inch in diameter passed through F horizontally, then through a 12-inch brick wall of the building, and were made fast to a large iron plate on the opposite side.

The stretching force was applied by means of a lever I. This consisted of a bar of the best tool steel, 4 feet long,  $\frac{3}{4}$  inch thick and  $2\frac{1}{4}$  inches wide. A steel knife-edge  $2\frac{1}{2}$  inches long was attached at right angles to the lever at its lower end. To the plate G was screwed another iron plate J, insulated from G by sheets of mica. The plate J had several horizontal notches cut in it, in which the knife edge on the lever could rest, serving as a fulcrum.

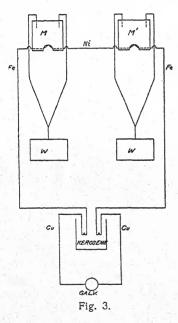
To hold the bar B from slipping and to afford a means of attachment to the lever, a friction clutch K, L was provided for each end. Each of these was constructed from two pieces of iron  $\frac{1}{2}$  inch thick, z inches wide and z inches long. These two iron blocks,

with a thin sheet of metal between them, were first securely bolted together by four  $\frac{3}{8}$ -inch steel bolts. A  $\frac{5}{16}$ -inch hole was then drilled lengthwise through the center. The sheet metal was removed and the bars ground with emery between the parts of the When tightly bolted together these clutches would not slip even when a tension was applied sufficient to break rods of steel. However, as a further precaution threads were cut for a half inch at each end of the bar and steel nuts screwed on outside the friction clutches. The clutch L was connected to the lever I by a link made of two pieces of strap iron I inch wide and  $\frac{3}{16}$  inch thick, one piece being placed on each side of the lever. Steel pins connected this link with the clutch and the lever. By means of the nuts on the rods H, the plate G could be moved parallel to itself and so adjusted that the lever always exerted a horizontal pull upon the bar. A box for carrying weights hung from the end of the lever and could be gradually lowered or raised by means of a jack-screw.

In order that the bar A might be under conditions as nearly as possible identical with those of B, its two ends were provided with a similar pair of friction clutches and lock-nuts. This was done in order that any changes in room temperature might produce the same effect upon the outer ends of the two bars.

To protect the bars from air currents, they were enclosed by a tight wooden box 12 inches wide, 9 inches high and 34 inches long, extending from the iron plate F to within two or three inches of plate G. The top of this box was hinged and could be lifted to afford access to the bars and glass windows in the top and side afforded means of observation.

Observations of temperature were made by means of thermoelectric couples. According to the method employed, it was not necessary to make measurements of temperature upon either bar, but merely to determine two points, one on each bar, which had the same temperature. Two thermo-electric couples made of No. 40 iron and nickel wire were mounted as shown in Fig. 3. M and M'are pieces of hard rubber from which are hung equal weights, Wand W'. These could slide along on the tops of the bars A and B. A piece of nickel wire connected M and M', passing through a small hole in each and ending in a loop. A piece of iron wire was similarly mounted on each side, the junction of iron and nickel coming directly on top of the bar. The iron wires passed out through holes in the bottom of the wooden box and were soldered to copper wires which ran to the galvanometer. The two junctions of iron and copper were immersed in a bottle nearly filled with kerosene. To avoid the possibility of thermo-electromotive forces being introduced at the connection with the galvanometer, the instrument was enclosed in a wooden box and the mirror observed through a small opening in the front. All parts of this enclosure were doubtless at



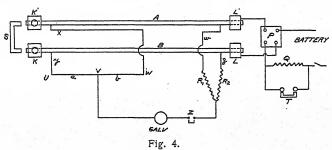
substantially the same temperature. Before each observation, the bottle of kerosene was thoroughly shaken to insure equality of temperature. It is therefore evident that if the two iron-nickel junctions are at the same temperature, the galvanometer will show no deflection. The couple on the bar B could be moved along in either direction by means of two prongs projecting at right angles to a light brass rod N which passed through the end of the box and the iron plate G. The galvanometer used was a four-coil Kelvin having the coils in parallel so that its resistance was about 6 or 7 ohms. The sensitiveness was such that

with the two couples at about 50 cm. from the copper clutch settings could be made to within about .2 mm.

To observe the relative position of the two couples, a white paper index was pasted to the top of each piece of hard rubber. A mirror O was mounted on a horizontal axis parallel to the bars above the window in the top of the wooden box. This served to throw the image of either index into the field of the telescope of a cathetometer mounted horizontally parallel to the bars. The windows in the box were kept covered except when readings with the cathetometer were being made.

To measure the elongation of the bar under tension, a telescope was mounted which could be moved horizontally by a micrometer screw reading to hundredths of a millimeter. This was focused simultaneously upon a scratch on the bar  $\mathcal{B}$  and a brass index securely clamped to  $\mathcal{A}$ . Since the whole frame yielded somewhat under stress the elongation was determined from the change in the distance between these two index marks. The probable error of setting on each mark was about .01 mm.

Heavy copper lead wires were soldered to the friction clutches L and L', while holes drilled in the tops of K and K' served as mercury cups through which the two bars A and B could be electrically connected by a piece of copper rod bent twice at right angles.



The arrangement of apparatus for the comparison of resistances is shown diagrammatically in Fig. 4. A number of storage cells could be connected with the two bars A and B through the commutator P. A resistance Q (consisting of two incandescent lamps in parallel) was introduced into the circuit. This resistance could be completely cut out by inserting the copper connector T in its mercury cups. After trying various forms of movable contacts, the fine lead wires x, y, s, w were finally soldered directly to the bars. Great difficulty was experienced in eliminating the effects of thermoelectromotive forces developed at various contacts of dissimilar metals. For this reason the lead wires were wherever possible made of the same material as the bars to which they were attached. The other ends of x and y were joined to the terminals of a slidewire bridge whose resistance wire a, b was wound on a revolving cylinder and the whole enclosed in a wooden box so that the three

junctions U, V, W should be at the same temperature. The free ends of z and were joined to the terminals of two standard resistance boxes  $R_1$  and  $R_2$ .  $R_1$  was keep fixed at 1,000 or 2,000 ohms while  $R_a$  was adjusted. Since it was found that small thermo-electromotive forces were developed by the pressure of an ordinary contact key, a key was constructed at Z consisting simply of a bent copper wire mounted in a piece of fiber on a spring and bridging the gap between two mercury cups. This insured always a certain and uniform contact and one free from any E.M.F. Adjustments of the sliding contact V and of the resistance  $R_2$  were made until the galvanometer showed no deflection whether the connector Swas in the mercury cups or removed. When S was removed T was also removed and a relatively small current employed. S was inserted T was also inserted and a current of from 10 to 20 amperes sent through the bars. In this way the resistance of the portion of B between y and z was compared with that of A between x and w. The direction of the current was then reversed by the commutator P and the measurements repeated. The results obtained by reversing the current seldom differed by more than one part in two thousand and in many cases no measurable difference could be observed.

#### THE OBSERVATIONS.

The procedure in making a set of observations was as follows: An electro-magnet connected with the program clock served to turn on the gas at any hour desired. Since four or five hours was required before the steady state was reached, the mechanism was usually set for three o'clock in the morning. The thermostat was adjusted to maintain the temperature desired in the experiment by setting the contact wire at the proper height in the tube. At eight or nine o'clock in the morning observations were usually begun. The thermo-electric couple on B was adjusted till the galvanometer showed no deflection and the position of the two couples read by the cathetometer. The relative position of the index marks on the two bars was read by the micrometer telescope. The electrical resistances of fixed lengths of the two bars were then compared. A suitable weight was then hung from the end of the lever and the apparatus left for at least an hour, or until observation

showed that the steady state was again reached. The series of observations was then repeated. This was continued till the maximum tension which the bar could safely stand was reached when the weights were gradually removed and the set of observations made with decreasing tension.

#### RESULTS.

Measurements have been made on bars of iron, steel, copper, brass and a few on aluminum and zinc. One typical set of measurements is given in full in Table I. In this and subsequent tables T

T		rometer adings.			Resistance.				
Kg.	A	B	=	B-A	Dir	ect.	R	eversed.	Ave.
0	mm. 2.50	mm. 2.50		mm. 0	199	9.0		1999.0	1999.0
40	3.95	4.90	-	.95	200	05.0	1	2005.2	2005.1
80	4.91	7.34	2	2.43	20	17.0	:	2018.0	2017.5
40	4.45	6.54		2.09	20	L2.0		2013.0	2012.5
· 0	3.33	4.63	16	L.30	200	03.0	1	2003.4	2003.2
Coup	les.		Z		2	K		Δs	σ
A	В	B-A	= 50 cm - [B-						
cm, 3.19	cm. 3.54	cm. .35	49.65	24	65	1.00	0	0	1.000
3.04	2.96	08	50.08	25	08	1.01	7	.000235	1.002
2.99	2.53	46	50.46	25	46	1.03	3	.000601	1.006
3.03	2.97	06	50.06	25	06	1.01	6	.000541	1.004
3.03	3.35	.32	49.68	24	-68	1.00	1	.000321	1.007

Length of bar between points from which  $\Delta L$  was measured, 111.5 cm. Length of bar between points from which resistance was measured, 85.4 cm. Value of Poisson's ratio employed in computing  $\Delta s_i$ , .277.

is the load in kilograms hung from the lever. Where the load is marked 0, the bars were stretched by a force due to the weight of the lever. This was equivalent to a load of about 5 kg. To express the tension in kilograms per square centimeter, T must be multiplied by 29.3  $\triangle L$  is the elongation in centimeters; l, the distance from the edge of the copper clutch to the position of the thermo-electric couple on bar B; K, the ratio of the thermal con-

ductivity of the bar to its conductivity before any tension was applied;  $\sigma$ , the corresponding ratio of specific resistances;  $\triangle s$ , the relative change in cross-section of the bar.

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TABLE II.

Further Measurements on B<sub>11</sub>.

T	$\Delta L$		σ	T	$\Delta L$	K	σ
	July 11, To	emp. 195°.			July 14, T	emp. 196°.	
Kg.	mm. 1.14	1.002	1.0009	Kg.	mm. 1.68	.9952	1.0019
40	2.00	1.018	1.0019	40	2.32	1.019	1.0030
80	2.85	1.022	1.0053	80	2.90	1.024	1.0047
40	2.40	1.007	1.0042	40	2.35	1.019	1.0031
0	1.61	1.000	1.0019	0	1.70	1.003	1.0017
	July 13, Te	mp. 196.5.			July 15, T	emp. 196°	
0	1.62	1.006	1.0019	0	1.70	1.003	1.0018
40	2.42	1.016	1.0042	40	2.36	1.022	1.0037
80	2.88	1.019	1.0044	80	2.95	1.030	1.0047
40	2.31	1.010	1.0031	40	2.35	1.022	1.0035
0	1.76	.9983	1.0020	0	1.79	.9972	1.0016

In computing the relative thermal conductivity no correction has been made for the decrease in cross-section of the bar as it is stretched. This change in cross-section may be computed from the value of Poisson's ratio for the given material and the correction applied. It is found, however, that it affects only the fourth decimal figure and hence is beyond the limits of accuracy of the experiment. Since the value of  $\sigma$  is computed to four decimal figures, the correction is there computed and applied.

In Table II. are given in condensed form the results of four other sets of measurements on the same iron bar  $\mathcal{B}_{\text{II}}$ , made after those given in Table I. The results for other bars of different metals are given in the other tables. Some of the results are plotted in the accompanying curves.

Many other measurements were made on other bars of the same metals, a total of eighteen different bars being employed. The results obtained for the other bars were substantially the same as those recorded. The difference in the behavior of different bars of the same metal was no greater than the difference in successive

TABLE III. Steel Bar, B<sub>10</sub>.

T	ΔL	K	σ	T	ΔL	K	σ	
	June 25, 7	emp. 201°	•	June 30, Temp. 205°.				
0	0	1.000	1.0000	0	.59	1.051	- 1.0018	
40	.43	1.034	1.0009	40	1.30	1.070	1.0018	
80	.88	1.050	1.0008	80	1.79	1.079	1.0021	
120		1.047		120	2.19	1.080	1.0022	
We	igh hung o	n over nigh	t.	175	2.85	1.076	1.0039	
-	June 26, Te	mp. 204°.		July 1, wt	t, hungon or	ernight. T	emp. 203°.	
175	2.42	1.050	1.0017	175	2.91	1.076	1.0028	
120	1.87	1.059	1.0023	120	2.11	1.064	1.0023	
80	1.35	1.057	1.0021	80	1.42	1.068	1.0018	
40	.74	1.056	1.0014	40		1.058		
0	.33	1.041	1.0012	0	.59	1.042	1.0009	
	June 27, T	emp. 204°.	MILES	July 2, Temp. 202°.				
0	.28	1.039	1.0004	0	.59	1.041	1.0014	
40	1.22	1.057	1.0010	40	1.31	1.063	1.0002	
80	1.69	1.071	1.0014	80	1.68	1.073	1.0012	
120	2.16	1.072	1.0020	120	2.06	1.078	1.0017	
175	2.69	1.069	1.0058	175	2.76	1.080	1.0028	
une 29 until Mon	, weight hu day. Temp	ng on from . 201°.	Saturday	July 3, 202°.	weight hung	g on over nig	ht. Temp.	
175	2.75	1.070	1.0056	175	2.76	1.085	1.0037	
120	2.01	1.062	1.0053	120	2.07	1.079	1.0034	
80	1.24	1.057	1.0050	80	1.43	1.071	1.0035	
40	.91	1.067	1.0044	40	1.04	1.070	1.0022	
0	.59	1.052	1.0027	0	.59	1.049	1.0013	

measurements on the same bar. The experiment has been set up twice with different apparatus and in all cases has yielded results of the same order of magnitude.

#### Conclusions.

It is probable that the apparent change in the thermal conductivity of the same bar under the same tension from day to day is due in part to changes in the character of the surface of the bar. No attempt was made to prevent oxidation, which affected somewhat the surfaces of both the bars compared. If the radiating power of one surface changed more than that of the other an apparent change in conductivity would result. It is hardly probable that this change

TABLE IV.

Copper Bar, B<sub>14</sub>.

T	ΔL	K	σ	T	$\Delta L$	K	σ
July 27, Temp. 152°.				August 4, Temp. 150°.			
0	0	1.000	1.0000	0	1.83	1.015	The second secon
30	1.63	1.026	1.0001	20	2.51	1.019	<u></u>
55	3.40	1.030	1.0010	30	2.74		g .
30	2.66	1.028	.9993	40	3.08	1.028	nce
0	1.74	1.020	.9985	55	3.40	1.016	sistance measured
	July 28, Te	mp 1520		40	2.98	1.026	Resistance not measured.
	July 20, 10	p. 132 .		30	2.76	1.018	~
0	1.67	1.024	.9985	0	1.98	1.013	
30	2.52	1.036	1.0000	August 5, Temp. 151°.			
55	3.67	1.030	1.0016		Trugust J,		•
30	2.97	1.037	.9999	0	1.96	1.010	
0	1.90	1.023	.9982	20	2.45	1.018	7
July 31, Temp. 150°.				30	2.60	1.015	Resistance not measured.
	July 01, 1	p. 150 .		40	2.96	1.014	sistance measured
0	1.92	1.021	÷	55	3.65	1.007	sta
30	2.75	1.032	i i	40	3.02	1.018	n n
55	3.14	1.024	eas	30	2.97	1.010	124
30	2.52	1.028	a	0	2.05	1.010	
0	1.83	1.018	log	-		4	
30	2.68	1.029	92	- 1			
55	3.52	1.020	tan	, X			
30	2.66	1.021	Resistance not measured.	100			
- 0	1.86	1.010	l &				

during the progress of a single experiment was sufficient to affect the comparison of these results among themselves. An inspection of the tables and the curves shows that in every case the thermal conductivity of the bars increases when a moderate tension is applied. As the limit of elasticity is reached this increase approaches a maximum. As the tension exceeds this limit, the conductivity remains practically constant in the case of the more elastic metals, such as steel and brass, or begins to diminish in the case of the softer metals. This is shown in some of the tests on iron bars and particularly in the case of copper. After a bar has been stretched its conductivity does not immediately return to its former value. This is most noticeable in steel and brass. In the softer metals the return to the original value is more perfect. It is probable that steel and brass would regain their original conductivity if given

TABLE V.

Brass Bar, B<sub>18</sub>.

 -							1
T	$\Delta L$	K	σ	T	$\Delta L$	K*	σ
	August 12,	Γemp. 156°	•		August 13,	Temp. 154	٥.
 	mm.				mm.		
0	0	1.000	1.0000	60	2.50	1.041	1.0099
30	1.46	1.027	1.0000	30	1.53	1.037	1.0077
60	2.19	1.030	1.0023	0	.83	1.024	1.0080
90	3.21	1.033	1.0047	-		rn ==4	
60	2.78	1.035	1.0012	August 14, Temp. 154°.			
30	1.94	1.025			mm.	·	
0	.92	1.015	1.0000	0	.74	1.020	1.0082
 				30	1.71	1.039	1.0094
August 13, Temp. 154°.			60	2.50	1.041	1.0100	
 			7.0006	90	3.19	1.038	1.0106
0	.81	1.021	1.0086	60	2.38	1.036	1.0096
30	1.88	1.037	1.0088	30	1.54	1.034	1.0097
60	2.60	1.041	1.0099	0	.71	1.018	1.0092
90	3.22	1.042	1.0102	0		2.010	1.5052

sufficient time, but this has not been tested by experiment. The total change in the conductivity of steel may amount to 7 or 8 per cent.; that of iron to 4 or 5 per cent.; brass, about 4 per cent. and copper 2 or 3 per cent. A few measurements were made on aluminum before the apparatus was put in its final form. These showed an increase in thermal conductivity of about one half per cent. under the maximum tension. Measurements were attempted upon bars of zinc but these proved unsatisfactory. The bars were not of uniform structure or cross-section, and stretched continuously and slowly under any weight applied, not being able to support even the weight of the lever. At the same time they showed apparently a larger increase in conductivity than bars of any other material tested. Since constant conditions were never attained, no great confidence can be placed in the results.

In every case the electrical resistance increased with increasing tension; that is, the conductivity diminished. These results are in substantial agreement with those obtained by other experimenters on the resistance of wires. Of course the conditions of this experiment were not suited to a highly accurate determination of this effect. It is, however, of interest to note that the changes in the thermal conductivity produced by moderate tensions are opposite in direction

to those in the electrical and are of an order of magnitude about ten times greater. Some rather rough experiments upon the effect of

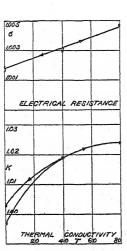


Fig. 5. Iron Bar  $B_{11}$  (July 14).

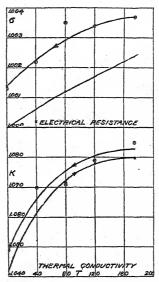


Fig. 6. Steel Bar B<sub>10</sub> (July 2 and 3).

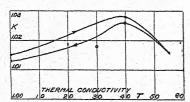


Fig. 7. Copper Bar B<sub>14</sub> (Aug. 4).

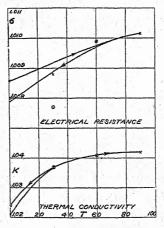


Fig. 8. Brass Bar B<sub>18</sub> (Aug. 13).

bending bars of iron and copper so that a large permanent deformation was produced seemed to show a marked decrease in thermal conductivity of from five to eight per cent. This is to be expected from the behavior of copper bars when stretched beyond their elastic limit. It is hoped at some future time to make a further study of this effect and also to investigate the changes produced by torsion.

My thanks are due to Mr. Walter Kachelski, the college mechanician, for advice and assistance in the construction of the apparatus.

OLIVET COLLEGE,

August 21, 1908.

## A STUDY OF OVERCAST SKIES.

By EDWARD L. NICHOLS.

In two recent communications I have described the results of certain measurements of the visible spectrum of the light from the sky 1 and have made comparisons between the spectrum of daylight and that of various artificial sources of illumination. 2 In the present paper, the spectrum of the light of overcast skies, is more particularly considered in its relations to the spectra obtained from the cloudless sky and from skies in intermediate stages.

As in the measurements already described the instrument used was a spectrophotometer of the Lummer-Brodhun type so arranged that one collimator pointed to the zenith while the other, which was horizontal, received the light from a comparison source of nearly constant intensity and composition. This comparison source was an acetylene flame. Measurements were made throughout the visible spectrum from the extreme red at .74  $\mu$  to the extreme violet at .38  $\mu$  thus including in the observations two regions lying close to the boundaries of the spectrum which had hitherto been comparatively neglected. The results obtained, as in the previous papers just referred to, are presented in the form of curves in which abscissæ are wave-lengths and ordinates give the brightness of the spectrum of skylight in terms of the brightness of the corresponding region in the spectrum of the acetylene flame. The scale adopted is entirely arbitrary. The brightness of the comparison spectrum was adjusted to a convenient intensity by the interposition of a diaphragm in front of the flame and of a milk glass screen of neutral tint, the nonselective character of the transmitting power of which had been ascertained by careful observation. Although many studies of the quality of the light from clear skies have been made, generally for the purpose of testing Rayleigh's theory but little attention has been given to the light of clouded skies. So far as I am aware in-

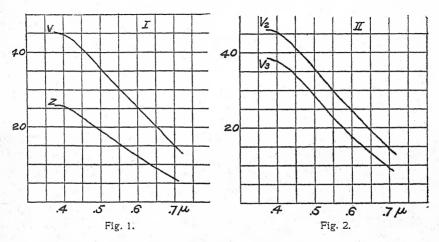
<sup>&</sup>lt;sup>1</sup> Nichols, Phys. Rev., Vol. XXVI., p. 497.

<sup>&</sup>lt;sup>2</sup> Nichols, Transactions of the Illuminating Engineering Society, Vol. III., p. 301.

deed the only definite spectrophotometric data are those published by Crova in the course of his extended and systematic observations on the skies at Montpellier in France.<sup>1</sup>

The results to be described in this paper were made during a vacation journey in Europe in 1907.

Measurements of the spectrum of the light from the zenith taken at times when the sky was completely overcast gave curves notable for their simplicity and for their similarity to one another. The type of these curves is sufficiently represented in Fig. 1 where the curve V is for an overcast sky studied in Vienna in June, 1907, and Z represents the character of the light obtained from a similar sky

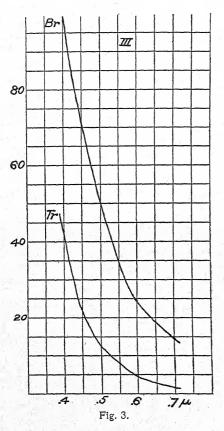


measured at Zell am See, Austria, in July of that year. The former curve was taken just before noon on a rather bright but completely cloudy day, the latter about 6 P. M. when the sky was heavily overcast and threatening rain. While these two skies differ in brightness approximately in the ratio of one to two they indicate remarkable similarity as to the composition of the light coming from the clouds.

It was noted by Crova in the course of his investigation that overcast skies differ but little in composition from many cloudless skies. This observation is verified by a comparison of the curves in Fig. 1 with those in Fig. 2 which are from measurements made at Vienna

<sup>&</sup>lt;sup>1</sup>Crova, Annales de Chimie et de Physique (6), XX., p. 480.

on a morning of a cloudless June day. It will be noted that curve  $V_2$ , Fig. 2, is almost identical with curve V, Fig. 1, and that  $V_3$  differs from these but slightly. All of these curves show the same characteristic, namely, a slight droop in the extreme violet. That the light from a cloud in shadow is ever identical in quality with that from blue skies is, I believe, contrary to the common impres-



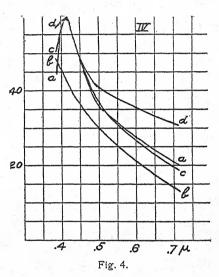
sion; yet it is frequently difficult to tell whether a portion of the sky towards which one is looking is clear or clouded unless one can detect the cloud structure.

While the spectrum of overcast skies is almost identical with that of certain cloudless skies the similarity does not extend by any means to all The intensely blue skies observed in fine weather in regions where the atmosphere is comparatively free from smoke and dust are of quite a different type. Measurements under such conditions give curves of which those in Fig. 3 are good examples. The curve Br is from measurements made at Brienz in Switzerland about 8 A. M. on a cloudless morning in

August, 1907, while the curve Tr was obtained at Trafoi in Tyrol before sunrise in July of that year. In these curves the relative brightness in the violet as compared with the red is several times as great as in the curves for overcast sky or in the curves for clear sky exhibited in Fig. 2. There is moreover no approach to a maximum at the violet end of the spectrum and the yellow and green are relatively very weak so that the curves are strongly concave.

Between these extreme types there exist numerous intermediate stages of the atmosphere which depend on the amount of condensed vapor which may be present. On a misty day, for example, when the sun is barely visible another and distinctive type of curve is obtained. Examples of this form are given in Fig. 4, the curves in which were taken at Zell am See on a misty day during which clouds were continually gathering and disappearing. Curve  $\alpha$  was

taken at 2:30 P. M. at which time no definite cloud forms were visible but the sky was full of white mist. At 2:45 P. M. the mist had cleared and the sky was blue and very Curve b represents bright. this condition and it is interesting to compare this curve with those in Fig. 2. The intensities are nearly the same as in  $V_a$ . The curve b is intermediate in type between  $V_2$  and the curves in Fig. 3 but much closer to  $V_2$  in character. 3:15 mist again filled the sky

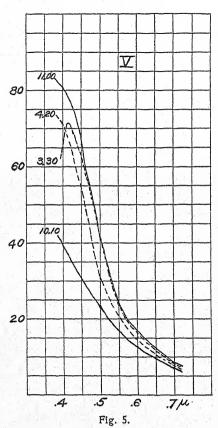


and curve c was obtained, the type of which corresponds in all respects with curve a. The intensities are the same throughout excepting in the extreme violet where measurements are at best more or less uncertain and both curves have the same characteristic maximum in the blue at .42  $\mu$ . This maximum is represented in reduced form in the slight droop in the curves from the overcast sky (Fig. 1) and is entirely absent in those obtained from cloudless skies of the type depicted in Fig. 3.

At times during the day in question the mists gathered into great masses of sunlit cumulus with patches of clear sky between. At a time when such a cloud mass filled the zenith curve d was obtained. In this curve the brightness of the extreme red of the spectrum at .7  $\mu$  is more than twice that of the spectrum of the clear sky shown in curve b. The intensity in the blue at .42  $\mu$  is the same as in

curves a and c but the peculiar maximum at this region is somewhat less marked.

This maximum in the blue, which is found in all spectrum curves for misty skies which I have observed, appears regularly as the day advances in the mountainous regions of Switzerland during fine summer weather when there is a gradual formation of mist in the upper atmosphere gathering into cloud masses with a tendency toward thunder showers in the afternoon. The change in the curve



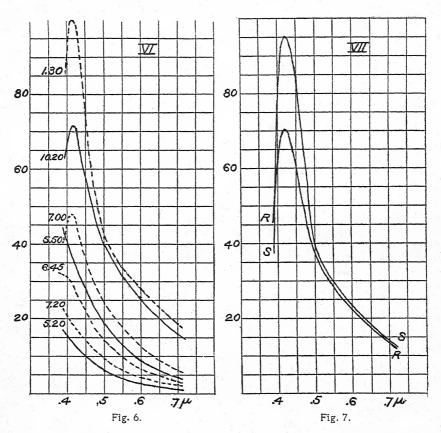
occurs before the presence of mist is easily observable to the eye. The maximum is commonly well established before noon and frequently persists until towards sunset.

The gradual growth and disappearance of this characteristic may be observed whenever observations are made at intervals throughout the day under weather conditions such as I have described. Fig. 5 shows results obtained at the top of the Brienzer Rothhorn in August, 1907. The curve taken at 10:10 A M. shows no trace of the maximum in the blue. At II A. M. the intensities in the blue and violet had rapidly increased and the approach to a maximum in this region began to manifest itself. At 3:30 P. M. the maximum was well

marked; at 4:20 P. M. it had again almost disappeared, the type of curve being almost identical with that obtained at 11 A. M. A much more complete series of observations showing these gradual changes of form during the day was obtained at Sterzing on July

17. Measurements were begun before direct sunlight reached the valley and were continued until after sunset.

The general character of the results are shown in Fig. 6 in which the curves drawn in full line are from measurements taken before noon while the dotted curves give data obtained in the afternoon. It will be noticed that the curves at 5:20 A. M. and 7 A. M. are of the usual early morning type and similar to those of Fig. 3. At



10:20 A. M., however, the maximum in the blue had developed and it persisted until late in the day. The curves at 1:30 P. M. and 5:50 P. M. show the continuance of this feature but at 6:45 P. M. it had nearly disappeared and at 7:20 P. M. was entirely gone. The curve at that hour had returned almost exactly to the form obtained before sunrise.

The maximum in the blue seems to occur in its most pronounced form at high altitudes. The best examples of it which I obtained were observed at Samaden in the upper Engadine and on the upper ice field of the Rhone Glacier.

In curve S, Fig. 7, which represents the readings taken at Samaden about 9 o'clock on a morning in July, when the sky appeared quite cloudless, the maximum is developed to an unusual degree. It will be noted that the spectrum of the light from the sky was relatively no brighter, compared with that of the acetylene flame, in the extreme violet at .38  $\mu$  than in the green at .50  $\mu$ . In the intervening region the ordinates rise however to double these values.

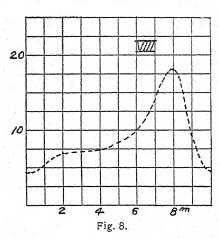
Curve R in Fig. 7 is from measurements made on the ice field of the Rhone Glacier at a point above the ice fall near which crossing is usually made from the Belvidere to the Naegeli Graetli. It was a bright morning but mists were continually forming on the surrounding peaks and melting away so as to leave the sky overhead apparently clear. It will be noted that the intensities of the spectrum throughout the region lying between .5  $\mu$  and .7  $\mu$  are almost identical with those obtained at Samaden. The variations lie almost entirely in the blue and violet of the spectrum. Although in these regions the curves do not coincide, the maximum at .42  $\mu$  appears in both.

Whether this highly variable band in the blue is an emission band superimposed upon the spectrum of a sky greatly diluted and whitened by the sunlight reflected from particles of condensed vapor; in which case it might be ascribed to the fluorescence of some variable component of the upper atmosphere, possibly ozone as suggested by Hartley; or whether it is wholly due to selective absorption in the ultra-violet on one side and in the green on the other, as seems much more probable, cannot be definitely determined from existing data. In any event it is a phenomenon absent from the clearest skies and one which is rapidly masked by the presence of considerable thicknesses of cloud-materials. Whatever be its nature it indicates an occasional departure from the distribution of intensities which characterizes the perfect sky of Rayleigh of a sort which demands further investigation.

It will be seen from the foregoing that there are between the

typical curves for the unclouded sky as exhibited in Fig. 3 and the curves for completely overcast sky (Fig. 1) a number of intermediate forms of considerable complexity. The presence of condensed vapor has the effect of increasing the intensity of the longer wave-

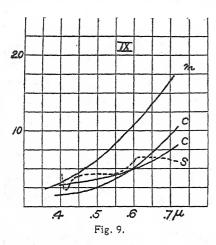
lengths of the spectrum so that the ordinates of the curves are raised throughout the red, yellow and green. At the same time the maximum in the blue is developed and the spectrum of light from the sky shows the phenomenon of selective reflection to a remarkable degree. Light from sun-illumined cloud masses exhibits the further modifications shown in curve d of Fig. 4 in which the intensities in



the red, yellow and green reach their highest values. The maximum in the blue is in this case still noticeable although by no means so marked as in the case of light from a clear sky in the presence of incipient mist.

That the brightness of the sky increases with the gathering of cloud masses up to the point where sunlight is completely shut out and the sky becomes thickly overcast is clearly shown by means of the results graphically recorded in Fig. 8. The readings from which this curve was plotted were all made from a single wavelength in the red end of the spectrum. The observations were taken during the rapid gathering of clouds upon a showery day, the initial condition being that of a blue sky with no visible mist. Measurements were made as rapidly as possible during the interval of ten minutes at the end of which the sky was completely and heavily overcast. The curve which has time as abscissæ counting from the first observation and intensities of the wave-length in question  $(.7 \mu)$ , in terms of that of the acetylene flame as ordinates, rises to a well-marked maximum after eight minutes and then falls to a value after ten minutes almost identical with the value of the

initial reading. The maximum corresponded as nearly as could be observed to the sudden exclusion of direct sunlight from the masses



of cloud under observation and the curve seems to indicate that up to the point where this occurred brightness increased rapidly as the mist gathered. Observations by Basquin 1 and others upon the illumination received from the sky under different conditions are quite in accord with the indications given in this curve. The brightest sky corresponds to a cloudy rather than a clear condition of the heavens but

after a certain density of the cloud masses has been attained the illumination falls off in consequence of the exclusion of direct sunlight from the visible surfaces of the clouds.

In the beginning of this paper I spoke of the curves obtained from overcast skies as being of a simple character by which is meant that there is less evidence of selective reflection than is the case from the open sky. The distribution of intensities is such as to indicate a composition of light closely related to that of radiation from the carbon in the comparison flame although of course of very much higher temperature. Nearly all measurements of light from unclouded skies, particularly at times when the surface of the earth, as well as the upper air, are in sunlight show on the other hand more or less well defined selectivity. A comparison of such curves with a curve for light from the sky taken upon a clear morning before sunrise - what I have called the typical dawn curve in the first of my previous papers already cited - shows a more or less complicated relationship like that represented in the curve s in Fig. 9. I have discussed the nature of these ratio curves in the paper in question. When, however, we plot similar curves for the ratios of overcast or mist-filled skies to the typical dawn curve, in cases

<sup>&</sup>lt;sup>1</sup> Basquin, Illuminating Engineer (N. Y.), Vol. I., p. 829.

where the fog is of sufficient density to prevent the direct illumination of the surface of the ground, we get curves of the form c and m in Fig. 9 which are quite free from the irregularities presented by the curve s. This would seem to indicate that the selectivity of ordinary sky-light is due on the one had to light reflected from the surface of the ground to the atmosphere and on the other to selective reflection which takes place in the upper layers of the atmosphere and which is cut out by the intervention of a layer of mist or cloud so that the light from overcast skies is more directly related to sunlight although modified as to the distribution of intensities than is the light commonly observed in the case of unclouded skies.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, June, 1908.

# NOTE ON THE SHORT-CIRCUITING OF CADMIUM CELLS.

132

By P. I. WOLD.

SEVERAL of the cadmium cells mentioned in a previous article have been short-circuited for different lengths of time to find the rate at which they recover and some of the recovery curves obtained are given below.

The period of short-circuiting varied from 15 seconds to 10 minutes and the general shape of the curves is the same in all cases and agrees very well with the curves obtained in a similar manner by F. E. Smith <sup>2</sup> and by Barnett.<sup>3</sup>

The internal resistance of these cells is about 1,500 ohms so that the actual current while short-circuited is rather small. The deviation from the normal value was obtained by a Wolff potentiometer, the short-circuited cell being placed in opposition to a cell taken as a standard and their differences read. Deviations from the normal were read directly to 1/100,000 of a volt and were estimated, with a fair degree of accuracy, to 1/10 of this.

The curves shown are typical curves out of a large number.

Fig. 1 shows the close agreement between two cells, 44 and 45, both short-circuited for 15 seconds. The cell 45 was short-circuited five times for a period of 15 seconds and the recovery curves were identically the same to within the width of a line.

Fig. 2 shows the effect of short-circuiting cell 44 different lengths of time. Curve I is for 15 seconds, curve 2 for 30 seconds, curve 3 for 60 seconds, curve 4 for 2 minutes, curve 5 for 5 minutes and curve 6 for 10 minutes.

In these two figures the axis OA represents the normal value of the E.M.F. of the cells and the ordinates represent the deviation from this normal in hundred-thousandths of a volt.

<sup>1</sup> PHYSICAL REVIEW, vol. 27, p. 329, 1908.

<sup>&</sup>lt;sup>2</sup> Philosophical Transactions of the Royal Society of London; Series A, vol. 207, p. 393.

<sup>&</sup>lt;sup>3</sup> Physical Review, vol. 18, p. 104, 1904.

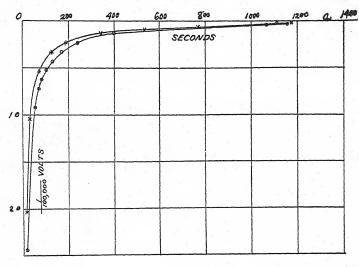


Fig. 1.

In his work Barnett subjected his cells to a much more severe test than in the present case, but apparently in this case the author was able to carry the measurements one place further in the decimal. Even with this increased accuracy in readings, the points, as plotted, fall remarkably close to the curve, indicating, to this degree of re-

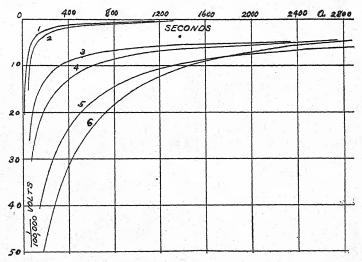


Fig. 2.

finement, a very definite and smooth recovery curve free from accidental disturbances within the cell itself.

An attempt to find a general form of equation for the recovery curve has, so far, been unsuccessful. The form suggests a logarithmic curve, but plotting logarithms of the deviation with time fails to give even an approximately straight line.

The general similarity of the decay curves in the case of phosphorescence, as shown by Professor Nichols and Merritt, with these recovery curves then suggested that these two effects might obey similar laws since in both cases the curve is probably determined by the reunion of free particles; in the one case probably electrons, in the other case the chemical ions which cause the polarization.

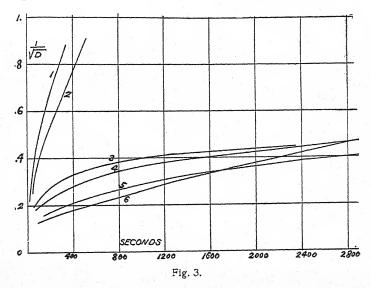
In their work on phosphorescence <sup>1</sup> Professors Nichols and Merritt have concluded that the curve obtained by plotting the reciprocal of the square root of the intensity with time is a straight line for small values of t and that it changes to a curve concave to the axis of t as t increases; but for larger values of t the relation between  $I^{-\frac{1}{2}}$  and t is again linear, the two straight portions merging into each other.

The results when the values of  $D^{-\frac{1}{2}}$  and t, as given in the curves of Fig. 2, were plotted as shown in Fig. 3, the numbers of these curves corresponding to the numbers in Fig. 2. In this case D represents the intensity or amount of polarization, i. e., the deviation of the cell from normal E.M.F. The curves agree in form surprisingly well with the corresponding curves shown by Professors Nichols and Merritt.

Because of the difficulties in obtaining readings in the very first part of the recovery it cannot be said at present that the first part of the above curves would also be straight lines with a different slope. Probably the shape of this curve is due to the fact that there are two, or more, effects giving or intensifying the polarization from which the cell must recover, and these individual recoveries are of different velocities. It may be that one phase of the recovery is brought about by the diffusion of ions, which at first are concentrated close to a separating surface in the cell, and the other part of the recovery is due to the reunion of these ions. At first probably

<sup>&</sup>lt;sup>1</sup> Physical Review, vol. 22, p. 279, 1906; vol. 23, p. 37, 1905.

the diffusion effect would be the predominant one, following one law, but later the chief effect would be that due to reunion of ions, which would follow a different law, similar perhaps to the law governing the reunion of electrons in the case of phosphorescence.



It may be, on the other hand, that we have simply the case of an excess of ions, producing polarization, at different points; as SO<sub>4</sub> ions near the cadmium and cadmium ions near or in the HgSO<sub>4</sub> and that the rate of recovery from these effects is different.

The author hopes to be able to do more work on this matter with the idea of determining with which case we have to deal.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

# THE DISPERSION OF ELECTRIC DOUBLE REFRACTION.

By T. H. HAVELOCK.

A RECENT paper by C. F. Hagenow, on electric double refraction in carbon bisulphide suggests a comparison of the experimental results with a formula which the present writer has given connecting the dispersion of artificial double refraction with the ordinary dispersion of the isotropic medium. In this connection the theory may be indicated briefly in the following manner.

In any medium the total electric displacement consists of two parts: (1) the æthereal displacement, measured by  $(4\pi)^{-1}$  times the electric force, (2) the material polarization of the particles constituting the medium. The latter part depends upon the effective electric force acting upon the particles, and this in turn depends for each particle upon the character and arrangement of the surrounding particles. We imagine an effective cavity to be associated with each particle, such that the force on the particle is the force within such a cavity in a medium uniformly polarized to the value of the material polarization vector at the point in question. For an isotropic medium the effective cavity is taken to be a sphere; as is well known, this leads to the formula

$$\frac{n_0^2 - I}{n_0^2 + 2} = \frac{4\pi}{3} \sum_{h} \frac{\alpha_h}{k_h^2 - k^2},\tag{I}$$

where  $n_0$  is the refractive index of the medium,  $2\pi/k$  is the period of the vibrations, and  $a_h$ ,  $k_h$  are constants assigned to each type of particle, the summation being extended over the various types. Suppose that the medium is subjected to mechanical stress, or to the action of an electric or magnetic field, so that it becomes doubly refracting; assume further that the consequent slight modification of the optical properties can be represented by a change of the effec-

<sup>&</sup>lt;sup>1</sup>C. F. Hagenow, Physical Review, vol. 27, p. 196, 1908.

<sup>&</sup>lt;sup>2</sup>T. H. Havelock, Proc. Roy. Soc., A., vol. 80, p. 28, 1907.

tive cavity from a sphere to an ellipsoid. Let the axes of the ellipsoid be in the ratios of  $1 + \varepsilon_1$ ,  $1 + \varepsilon_2$  and  $1 + \varepsilon_3$ ; also let  $n_1$ ,  $n_2$ ,  $n_3$  be the principal refractive indices of the medium.

The components of effective force within the cavity can be evaluated and we obtain, instead of (1), three equations of the type

$$\frac{{n_1}^2 - 1}{{n_1}^2 + 2 + 3s_1({n_1}^2 - 1)} = \frac{4\pi}{3} \sum_{h} \frac{a_h}{k_h^2 - k^2}$$
(2)

where

$$S_1 = -\frac{4}{15}\varepsilon_1 + \frac{2}{15}(\varepsilon_2 + \varepsilon_3).$$

Hence from (1) and (2) we can find expressions for the principal indices in terms of  $n_0$ , the refractive index of the isotropic medium composed of the same particles in equal density.

If the strained medium behaves like a uniaxial crystal, we have

$$n_1 = n_0 - \frac{2}{15} \frac{(n_0^2 - 1)^2}{n^0} \varepsilon$$

$$n_2 = n_0 + \frac{1}{15} \frac{(n_0^2 - 1)^2}{n_0} \varepsilon.$$

Hence the dispersion of the double refraction, measured by the difference of the ordinary and extraordinary indices, is given by

$$\delta \propto \frac{(n_0^2 - 1)^2}{n_0} \tag{3}$$

This formula connects the dispersion of the slight artificial double refraction with the ordinary dispersion of the isotropic medium. The relation suggested by Kerr as the result of experiments was, that the double infraction induced in CS<sub>2</sub> by an electric field was inversely proportional to the square root of the wave-length, but this has been disproved by the experiments of Blackwell, and again by those of Hagenow. In the paper already quoted, the writer has shown that the formula (3) agrees well with Blackwell's results; this is also the case for the more recent data, as is shown by the following table. The first two columns give the experimental data which are taken from Hagenow's paper; these are the average results of sets of observations and it is claimed that the experimental error is small,

<sup>&</sup>lt;sup>1</sup> H. L. Blackwell, Proc. Amer. Acad., vol. 41, p. 650, 1906.

except that the value of  $\delta$  for  $\lambda$  equal to 500 appears to be abnormally low and the value of  $\lambda$  equal to 700 is also not so reliable. The values for  $n_0$  given in the third column were obtained by the help of the table given by Martens, using also a temperature correction of  $-9 \times 10^{-4}$  for each degree rise in temperature; we obtain thus values correct to three decimal places. The fourth column shows the values of  $\delta n_0/(n_0^2-1)^2$ , which ought to be constant by relation (3); omitting the values at 600 and 700 for the reasons stated above, we have a mean value of 60.57 for the remaining six values, showing a maximum divergence from the mean of about .6 per eent.

CS, at 25°.

λ	δ obs.	$n_0$	$\delta n_0/(n_0^2-1)^2$
430	116.2	1.672	60.27
450	112.5	1.662	60.22
500	106.8	1.643	60.75
550	102.1	1.630	60.60
590	100	1.623	60.78
600	97.5	1.621	59.68
650	97.1	1.614	60.83
700	96.7	1.610	61.42

A preliminary account of investigations on the magnetic and electric double refraction of nitrobenzene has recently been published by Cotton and Mouton.<sup>2</sup> This liquid is interesting on account of the double refraction being extremely large compared with that of CS<sub>2</sub>; a series of observations is given showing the magnetic double refraction at various wave-lengths and it is stated that electric double refraction of the same order was obtained. Owing to the present lack of more exact data both for the double refraction and for the ordinary dispersion of nitrobenzene under similar conditions it is not possible to compare the formula given above with these results.

As a result of their series of experiments on magnetic double refraction, dealing originally with the Mayorana effect in colloidal solutions, Cotton and Mouton believe that the phenomena are due to orientation of particles, and they suggest a similar explana-

<sup>&</sup>lt;sup>1</sup> Martens, Annalen der Physik, vol. 6, p. 632, 1901.

<sup>&</sup>lt;sup>2</sup> Cotton and Mouton, Comptes Rendus, t. 147, p. 193, 1908.

tion for the electric double refraction in nitrobenzene, namely, orientation of the molecules. In the theory sketched above, an essential point is in regarding the effective cavity to be changed from a sphere to an ellipsoid by the impressed field. Now this may be due to an orientation of similar æolotropic particles, if we regard the isotropy of the unstrained medium as an average effect of orientation of the particles in all possible directions; or it may be due to a rearrangement in grouping of an assemblage of similar particles. In deducing the relation (3) given above, the latter hypothesis was used, and we have seen that the formula is supported by the experimental data available at present.

Whether a similar formula could be obtained on the hypothesis of orientation or not, it seems desirable to have as far as possible parallel series of observations on the dispersion of the artificial double refraction and the ordinary dispersion of the isotropic medium taken under similar conditions, for instance as regards temperature and purity of materials.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE, November 6, 1908.

### **PROCEEDINGS**

OF THE

# AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FORTY-FIFTH MEETING.

A JOINT meeting of the Physical Society and Section B of the American Association for the Advancement of Science was held in the Physical Laboratory of Johns Hopkins University, Baltimore, Md., December 28-31, 1908.

The President of the Physical Society, Edward L. Nichols, and the Vice-President of Section B, Karl E. Guthe, presided at alternate sessions.

At the afternoon session of Tuesday, December 29, the retiring Vice President of Section B, Dayton C. Miller, delivered an address on The Influence of the Material of Musical Instruments upon the Quality of the Sound produced.

At the business meeting of the Physical Society, held Wednesday afternoon, December 30, 1908, the following officers were elected for the year 1909: Henry Crew, President; W. F. Magie, Vice-President; Ernest Merritt, Secretary; J. S. Ames, Treasurer; J. C. McLennan, Ernest F. Nichols, Members of the Council.

The following papers were presented:

Fatigue of Metals Excited by Roentgen Rays. L. T. MOORE and R. E. C. GOWDY.

Errors in Magnetic Testing of Ring Specimens. M. G. LLOVD.

Data regarding Recent Magnetic Storms. L. A. BAUER.

Optical Properties of Electrolytic Films of Iron, Nickel and Cobalt. C. A. Skinner and A. Q. Tool.

An Absolute Gauge for Measuring High Hydrostatic Pressures. P. W. Bridgman.

The Resistance of Mercury as a Secondary Gauge for High Pressures. P. W. BRIDGMAN.

Methods for Measuring Compressibilities at High Pressures. P. W. BRIDGMAN.

An Experimental Determination of the Terminal Velocity of Fall of Small Spheres in Air. John Zeleny and L. W. McKeehan.

Note on the Effect of the Phase of Harmonics in Sound Waves. M. G. LLOYD and P. G. AGNEW.

Magnetic Double Refraction Normal to the Field in Liquids. C. A. Skinner.

The Absorption Spectra of Various Potassium and Uranyl Salts in Solution. HARRY C. JONES and W. W. STRONG.

New Series in the Spectra of Ca, Sr and Ba. F. A. SAUNDERS.

Ionization in Closed Vessels. W. W. STRONG.

Velocity of the Negative Ions Produced by Ultra-violet Rays in Various Gases at Different Pressures and Temperatures. Alois F. Kovarik.

Momentum Effects in the Electrical Discharge. F. E. NIPHER.

Electrical Stimulation of Plant Growth. Amon B. Plowman.

Note on the Kathode Equilibrium of the Weston Cell. F. A. Wolff. The Theory of Coupled Circuits. Louis Cohen.

Photographic Registration of Sounds. DAYTON C. MILLER.

The Effect of the Magnetic Impurities in the Copper Coils of Moving Coil Galvanometers upon their Sensitiveness, Hysteresis and Zero Shift. Anthony Zeleny.

The Three Temperature Coefficients of the Moving Coil Galvanometer and their Relation to the Temperature Coefficients of its Various Parts. Anthony Zeleny and O. Hovda.

A New Method for the Absolute Measurement of Resistance. E. B. Rosa.

A Plea for Terrestrial and Cosmical Physics. L. A. BAUER.

The Ellipticity of the Earth is Not a Proof of a Former Liquid State. John F. Hayford.

Atomic Theories. L. T. MORE.

The Dynamophone. J. BURKITT WEBB.

An Electrical Method for Determining the Amount of Moisture in Grain and Other Materials. Anthony Zeleny.

On the Extra Transmission of Electric Waves. F. C. BLAKE.

Entladungsstrahlen. ELIZABETH R. LAIRD.

A Spectrometer for Electromagnetic Radiation. A. D. Cole.

A Method of Determining the Electrode Potentials of the Alkali Metals. G. N. Lewis and C. A. Kraus.

Non-Newtonian Mechanics and the Principle of Relativity. G. N. Lewis and R. C. Tolman.

On the Influence of Temperature and of Transverse Magnetization upon the Electrical Resistance of Bismuth and Nickel. F. C. BLAKE.

A New Form of Standard Resistance. EDWARD B. ROSA.

A Proposed Modification of the Kirchoff Method for the Absolute Measurement of Resistance. Frank Wenner.

An Instrument Designed for More Precise Determination of the Magnetic Declination at Sea. W. J. Peters.

The Electric Conductivity of the Atmosphere over the Pacific Ocean. PAUL R. DIKE.

The Ultra Violet Absorption and Fluorescence and the Complete Balmer Series of Sodium Vapor. R. W. Wood.

Results of Recent Intercomparisons of Magnetic Standards by the Carnegie Institution. J. A. Fleming.

Some Optical Effects of Changes in Ether Density. (By title.) Chas. F. Brush.

The Thermodynamics of Saturated Vapors. (By title.) J. E. SIEBEL.

The Heat Balance in Thermoelectric Batteries. (By title.) J. E. SIEBEL.

The Lumeter, a Practical Measure of General Luminosity. (By title.) HENRY E. WETHERILL.

A Critical Review of the Problem of Pressure in the Kinetic Theory of Gases. L. D'AURIA.

Arc and Spark Phenomena in the Secondary of a High Potential Transformer. (By title.) E. S. JOHNNOTT.

On the Diurnal Viarations in the Intensity of the Penetrating Radiation Present at the Surface of the Earth. G. A. CLINE.

On the Character of the Radiation from Potassium. J. C. McLennan. The Action of Electrolytes on Copper Colloidal Solutions. E. F. Burton.

The Upper Inversion in the Atmosphere. W. J. Humphreys.

Some Remarks on Solar Magnetism. W. J. Humphreys.

Note on Thermoluminescence. ELIZABETH R. LAIRD.

The society passed a vote of thanks to the authorities of Johns Hopkins University, and especially to the members of the department of physics, for the many courtesies extended to the Society during the meeting.

Adjourned Thursday, December 31, 1908, at 5 P. M.

ERNEST MERRITT, Secretary.

### A HIGH TEMPERATURE REGULATOR.1

### By H. M. RANDALL.

THE variation in the temperature of the oven is detected by a thermo-couple or a platinum thermometer. The coil of the galvanometer in the potentiometer or the Wheatstone Bridge circuit is provided with a light aluminum boom, b. With rise of temperature this boom moves between two spring jaws, s, which open and close upon one another regularly, the movement being caused by the rotation of the cylinder, C, provided with the elevations, p. C is driven by a motor at

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

low speed. The platinum contact strips, K, are insulated by hard rubber blocks from the steel springs, s, and just escape contact with each other when the boom is not between them. The diameter of C is such that the springs, s, pinch the boom with considerable force when it is between them in the position shown in the figure, thus completing a battery circuit containing an electro-magnet; this latter, responding, shunts

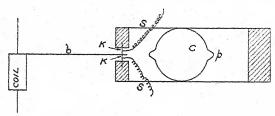


Fig. 1.

part of the heating current of oven. As the oven cools the boom moves from between the jaws through its zero positions to a second similar pair of jaws on the opposite side, which operate to open the shunt circuit. With proper adjustment no strain is put upon the galvanometer suspensions when the jaws close upon the boom: thus light suspensions may be used. With this arrangement it has been possible to maintain for hours temperatures in the neighborhood of 1000 °C. in the oven employed, without any variation in temperature occurring which could be detected by a couple, a Siemans and Halske potentiometer being used.

THE ABSORPTION SPECTRA OF VARIOUS POTASSIUM AND URANYL SALTS IN SOLUTION.<sup>1</sup>

BY HARRY C. JONES AND W. W. STRONG.

THE methods used in this work are practically those described by Jones and Anderson in publication number 110 of the Carnegie Institution of Washington.

Potassium ferricyanide in aqueous solution was found to obey Beer's law for dilutions ranging between normal and 1/4096 normal.

The limit of absorption was very sharp. Three weak bands at  $\lambda\lambda$  3220, 3000 and 2550 were found.

Potassium ferrocyanide in aqueous solution was found to obey Beer's law between concentrations ½ normal and 1/128 normal. Potassium chromate in water obeys Beer's law between the ranges of concentration 2 normal and 1/2048 normal, potassium dichromate between ½ normal and 1/1536 normal.

<sup>1</sup>Abstract of a paper presented at the Baltimore meeting of the Physical Soc ety, December 28-31, 1908.

The uranyl salts investigated have been the nitrate, sulphate, acetate, chloride and bromide. Beer's law was not found to hold except for dilute solutions. Water, methyl and ethyl alcohols have so far been used as solvents. The absorption is greater in each case in the more concentrated solutions (the amount of salt acting as absorbing agent being the same) except in the remarkable case of the acetate in water.

The absorption spectra consist of at most twelve bands in the blue violet region, the number of bands depending upon the amount of uranyl salt in the solution. The positions of the uranyl nitrate bands are all shifted towards the violet with reference to the bands of the other salts. This does not agree with the results given by other workers. Keeping the amount of salt the same and diluting the solution did not cause any change in the positions of the bands.

Dehydrating agents like aluminium chloride and calcium chloride cause the bands to shift towards the red. It is probable that hydration has some influence on this shifting of the bands, since uranyl nitrate possesses much more water of crystallization than any of the other salts.

The wave-lengths of the uranyl bands are different in methyl and ethyl alcohol solutions from what they are in water. This investigation is being carried out with the aid of a grant from the Carnegie Institution of Washington.

### IONIZATION IN CLOSED VESSELS.1

By W. W. STRONG.

URING the past summer work upon ionization in closed electroscopes was continued. Among the electroscopes used was one whose calibration curve is given on page 44 of the July Physical Review. The rate of leak was found in a cistern as described in that article. The leak September, 1907, was slightly (5 to 10 per cent.) less than in July, 1908, in the same cistern under the same conditions. A daily variation with a maximum at noon was shown for the electroscopes in the open. The above would indicate that for over a year the natural ionization in the electroscope was practically constant.

Experiments were made to test whether direct sunlight affected the ionization current within an electroscope. Curved electrode electroscopes made of glass were used. The glass was wrapped with fine wire so as to destroy any electrical induction on the gold leaf by external bodies. The effects of air currents and radiometric action is very great but by exposing to sunlight for several hours and then darkening the room for an hour, these difficulties can be partly surmounted. The results indicated that direct sunlight does not increase the rate of leak to any considerable amount.

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

# An Absolute Gauge for Measuring High Hydrostatic Pressures.<sup>1</sup>

By P. W. BRIDGMAN.

IN practically all forms of gauge for measuring high pressure the weight is determined which when acting on a piston of known cross-section exactly balances the action of pressure on the other end of the piston. This piston moves freely without friction in an outer cylinder, which it fits so accurately that the rate of leak is very slow. The cylinder is subjected to pressure on the interior only, the effect of which is to increase the inner diameter of the cylinder as the pressure increases. The piston is, on the other hand, subjected to pressure on the exterior curved surface, and therefore loses in diameter with increasing pressure. The effect of the simultaneous swelling of the cylinder and contraction of the piston is a widening of the crack between piston and cylinder under increasing pressure, thus increasing the rate of leak and putting a speedy limit to the pressure range accessible to the instrument. The manometer of Amagat is probably the best known form of this gauge. The pressure limit of the gauge in Amagat's hands was about 3000 kgm. per sq. cm.

In the form of high pressure gauge described in this paper, the above mentioned source of leak is obviated by such a disposition of packing that the cylinder in which the freely moving piston plays is subjected to pressure on the exterior as well as on the interior surface. The effect of the application of pressure to the exterior of the cylinder is to decrease the interior diameter with increasing pressure, thus decreasing the width of the crack through which leak occurs. By properly varying the disposition of the packing the rapidity of the leak may be controlled. The rapidity of the leak is further decreased in this type of gauge by decreasing the dimensions below the customary values. The diameter of the piston used in this gauge was only 1.6 mm., as against 6 mm. used by Amagat. With this gauge pressure of 6,800 kgm. per sq. cm. have been measured repeatedly without perceptible leak. Comparison of two such gauges with each other indicates a probable accuracy of at least one tenth per cent. in the absolute pressure measurement over the entire pressure range, with a sensitiveness at the maximum of about 3 kgm. per sq. cm. The correction which must be applied for the elastic deformation of the metal of the gauge amounts at 6,800 kgm. to only one fifteenth per cent.

<sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, Debember 28-31, 1908.

The Resistance of Mercury as a Secondary Gauge for High Pressures.<sup>1</sup>

By P. W. BRIDGMAN.

In the preceding abstract, an absolute gauge for hydrostatic pressures up to 6,800 kgm. per sq. cm. was described. In practical use it is inconvenient, because of its bulkiness and the time necessary to make a single measurement. The more common forms of secondary gauge in ordinary use, while undoubtedly more convenient, yet show rapidly increasing sources of error as the pressure is pushed to values as high as the above. The chief of these sources of error is the entrance of hysteresis effects. Another convenient form of secondary gauge proposed by de Forest Palmer in 1897 employs the variation of electrical resistance of mercury. Measurements were made by de Forest Palmer to 2,000 kgm. with a probable error of about 1.6 per cent. in the pressure which might be deduced from the resistance measurement.

In this paper the suitability of the mercury gauge has been investigated over a wider pressure range and with somewhat greater accuracy. It was found that the gauge shows no hysteresis and is capable of giving the pressure to 6,800 kgm. with an accuracy of one tenth per cent. The greatest source of error in actual use is the irregular action of the glass capillary containing the mercury. The glass must be seasoned by repeated subjection to pressure before its indications become regular. The glass must be reseasoned if subjected to large changes of temperature. It was found that an easily fusible glass in which the strains left from drawing are small gives the most regular results. The glass employed was Jena tubing No. 3880a, and it is recommended that this tubing be used if this form of gauge should be employed elsewhere. An empirical formula is given connecting the change of resistance in a capillary of the above glass with the pressure correctly to one tenth per cent. over the pressure range 500-6,800 kgm.

From the compressibility of the glass and of the mercury, which will be determined in another paper, the change of specific resistance of mercury is determined from the apparent change in the above glass envelope. The changed specific resistance corrected for the changed density is also determined. Empirical formulas are given connecting these two resistances with the pressure, but no theoretical discussion of the significance of this change has been attempted.

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

METHODS FOR MEASURING COMPRESSIBILITIES AT HIGH PRESSURES.<sup>1</sup>

By P. W. BRIDGMAN.

In this paper, methods are described for measuring the linear compressibility of solids in the form of rods and the cubical compressibility of liquids. The pressure which went to 6,500 kgm. per sq. cm. was measured with the mercury resistance gauge described in a preceding abstract. The motive in collecting the data was merely the bearing that they have on the variation of the specific resistance of mercury. No determination of compressibilities that might be interesting in themselves was attempted.

Two methods were used for determining the linear compressibility of solids; a comparative method for relatively highly compressible solids like glass, and an absolute method for incompressible solids like steel. In the first method a tube of glass fits into the comparison tube of steel. These are kept permanently in contact at one end, while at the other end there is a ring sliding on the glass and in contact with the end of the steel stube. Fluid pressure is applied all over both steel and glass, producing a displacement of the free end of the glass with respect to the steel. This displacement is indicated by the shift of the brass ring, which can be measured after pressure is released. In the second method, the rod of steel or other substance is placed in a heavy cylinder subjected to pressure on the interior. The effect of this interior pressure is to shorten the steel rod, and to simultaneously lengthen the cylinder. The relative change of length of rod and cylinder is indicated by a ring sliding on the rod like the ring on the glass above, while the absolute change of length of the cylinder is measured from the outside. The difference of these two changes of length gives the absolute change of length of the steel By these methods the linear compressibility of two kinds of glass, of aluminum, and of several grades of steel were determined. The compressibility of the glass shows intrinsic irregularities of perhaps five per cent. Large changes in the carbon content of the steel were found to make very slight changes in compressibility. To test the justifiability of the hypothesis that solids are equally compressible in all directions, two specimens of boiler plate were measured, cut along and perpendicular to the direction of rolling. There was no difference of more than the experimental error, one tenth per cent.

The method for measuring the compressibility of mercury was a revival of an old method due to Perkins in 1826 and since allowed to fall into disuse because of the inaccurate results obtained by him. A freely moving piston is forced by fluid pressure into a steel cylinder containing the mercury. The displacement of the piston is indicated by a sliding ring

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

similar to the above. From this displacement of the piston and the compressibility of the containing vessel of steel, which may be determined as above, it is easy to calculate the volume compressibility of the mercury. The probable error of this determination was estimated to be about one third per cent. The change of compressibility with pressure is less according to this determination than that found by Carnazzi, who worked to 3,000 kgm., and who made the only previous determination with which these results can be compared at more than 500 kgm.

The values found for the cubic compressibility were as follows:

Jena glass No. 3880a, 2.17  $\times$  10<sup>-6</sup> kgm./cm.<sup>2</sup>,

Jena glass No. 3883,  $2.23 \times 10^{-6} \text{ kgm./cm.}^2$ ,

Steel varied from  $5.16 \times 10^{-7}$  to  $5.30 \times 10^{-7}$  kgm./cm.,

Aluminum rod, 11.7  $\times$  10<sup>-7</sup> kgm./cm.<sup>2</sup>.

Volume of mercury is connected with pressure by the relation:

$$\Delta V/V_0 = ap + bp^2,$$

where

$$\log a = 4.5681 - 10,$$
$$\log (-b) = 9.2977 - 20.$$

THE JEFFERSON PHYSICAL LABORATORY, CAMBRIDGE, MASS.

FATIGUE OF METALS EXCITED BY ROENTGEN RAYS.<sup>1</sup>
BY LOUIS T. MORE AND R. E. C. GOWDY.

THE work is a continuation of the results previously obtained in the same subject (Phil. Mag., 1907, and Chicago meeting of the American Association for the Advancement of Science). A new method has been devised for measuring the secondary radiation given off by metals bombarded by X-rays. Previous results have been confirmed and extended.

To account for the secondary radiation, Professor J. J. Thomson has advanced the theory that the X-rays effect a disintegration of the atomic structure of the metal and permit the expulsion of charged corpuscles. Our experiments make this theory doubtful. Iron, lead and copper plates with pure surfaces were used and then the plates were coated with thin films of the lower oxides of the metal and again with films of the higher oxides. The effect of this successive oxidation on the fatigue seems to show that chemical changes of the surface produced by the X-rays with the consequent changes of surface electrified double layers will account for the phenomena observed.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

# A METHOD OF DETERMINING THE ELECTRODE POTENTIALS OF THE ALKALI METALS.<sup>1</sup>

By GILBERT N. LEWIS AND CHARLES A. KRAUS.

HE electrode potentials of the metals of the alkalies and the alkaline earths, notwithstanding their great importance, have never been determined, because of the extreme reactivity of these metals. The method now adopted, which has proved entirely successful in the case of the sodium e ectrode, consists in measuring the electromotive force between the metal and its dilute amalgam in mercury with an electrolyte consisting of a solution of a salt of the metal in question in liquid ethylamine. The electromotive force so obtained can readily be shown to be independent of the electrolyte and the solvent used. It is therefore the same as would be obtained if the electromotive force between the metal and amalgam could be measured in an aqueous solution. The potential of the amalgam against a normal solution of a salt of the metal in water may, with certain precautions, be measured directly against a normal electrode. Adding the electromotive force so obtained to the electromotive force between the metal and amalgam, gives directly the potential of the metal in a normal solution of its ion in water, the potential of the normal electrode being taken as zero. In the case of sodium, this method has made it possible to determine the electrode potential within a few tenths of a millivolt. The value obtained is about half a volt higher than that which has been previously assumed for the sodium electrode.

ULTRA-VIOLET ABSORPTION AND FLUORESCENCE AND THE COM-PLETE BALMER SERIES OF SODIUM VAPOR.<sup>1</sup>

By R. W. Wood.

THE absorption spectrum of dense sodium vapor, contained in a steel tube I meter in length, provided with quartz windows, and heated red hot in a combustion furnace, shows the lines of the principal series (Balmer formula) reversed. But seven lines of this series have been previously observed, the observations having been confined to the emission spectrum.

Employing a small quartz spectograph by Fuess (focus only 15 cm.) twenty four lines were found and measured and indications of the "head" of the series appeared in the plate though it was not resolved into lines.

With the large quartz spectograph of the Bureau of Standards 48 lines were resolved, bringing us within 0.1 of an Ängstrom unit of the theoretical head of the band. The largest number of lines forming a Balmer

<sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

series ever observed in the laboratory is twelve in the case of hydrogen (Cornu and Ames). Solar hydrogen (chromosphere spectrum) shows 29 lines. The sodium series is thus nineteen ahead of any Balmer series ever observed, even in celestial sources. Higher resolving power would doubtless resolve more lines, and the only limit appears to be set by the vapor density and the power of the spectroscope. These ultra-violet lines are accompanied on each side by a channelled spectrum, analogous to the channelled spectra observed in the vicinity of the D lines, which form the first member of the Balmer series.

It is in the region of the channelled spectra that the interesting results of the fluorescence of the vapor previously described were found. attempt was accordingly made to ascertain if the ultra-violet channelled spectra exhibited the same phenomenon. Such was found to be the case. Exciting the vapor with the zinc spark, a strong fluorescence was found to be stimulated by the zinc triplet at wave-length 3344-3302. This triplet is in coincidence with the second line of the Balmer series. at the middle of the accompanying channelled spectrum. A strong fluorescence banded spectrum was found extending from the triplet up to wave-lengh 3630, strongest at wave-length 3612, decreasing in intensity on each side of this point. No fluorescence appeared below the zinc triplet. Exciting with the zinc triplet separated by the spectroscope, we find no visible fluorescence. Exciting with visible light we find no trace of the ultra-violet fluorescence, which indicates that the effect is not carried over from one channelled spectrum to the other. Experiments with other sources of ultra-violet light are in progress.

# Non-Newtonian Mechanics and the Principle of Relativity.<sup>1</sup>

By GIFFORD N. LEWIS AND RICHARD C. TOLMAN.

THE laws of Non-Newtonian Mechanics previously derived by one of the authors from the fundamental conservation laws and from a simple assumption in regard to the nature of light, are identical with those which Einstein has obtained from the principal of relativity and the laws of electro-dynamics. In this paper it is shown that the same equations may be obtained without the aid of the electro-magnetic theory from the principle of relativity and the conservation laws.

<sup>&</sup>lt;sup>1</sup>Abstract of a paper presented at the Baltimore meeting the of Physical Society, December 28-31, 1908.

### PHOTOGRAPHIC REGISTRATION OF SOUNDS.1

BY DAYTON C. MILLER.

POR making large scale records, showing the details accurately, of complex sound waves having frequencies ranging from 500 to 10,000, the phonograph and oscillograph methods seem unsuitable. The following direct mechanical method has given satisfactory results.

A small steel cylinder, r mm. in diameter, is arranged to receive angular motion, with a minimum of reaction effects, which is proportional to the displacement of a sensitive diaphragm. A minute mirror, with its plane in the axis of the cylinder, reflects light to a special camera, and at a distance of 30 cm. gives waves 15 cm. wide which show great detail. Results were exhibited.

### NOTE ON THERMOLUMINESCENCE.1

BY ELIZABETH R. LAIRD.

THEORY suggests that in the case of thermoluminescent salts the change producing luminescence goes on very slowly at ordinary temperatures and is merely accelerated by raising the temperature. An additive method for obtaining the effect of thermoluminescence should therefore show its existence at room temperatures.

This was tested by wrapping up photographic plates for different periods of time with the sensitive film towards some thermoluminescent salt and developing later, at the same time heating the salt to observe the remaining thermoluminescence.

The salts used were a solid salt solution of calcium sulphate and manganese sulphate, the same with an undetermined admixture due to which the thermoluminescence was brighter in patches and was restored in these patches after heating by exposure to light, and calcium sulphide which had been kept in the dark some time after all visible luminescence had ceased.

The results showed that in each case the photographic plate was affected, that where the thermoluminescence was strong as was the case with the second and third salts used if they had been exposed in strong daylight, the effect was obtained in less than two weeks or even in a few days, that when the thermoluminescence was faint as when calcium sulphide was exposed only to dim light a period of two months was required for a marked effect, and that this was also the case with the first named salt solution. Where the effect was uneven the greater effect corresponded to the portions showing brighter thermoluminescence.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

Control plates used with salt that had not been exposed to light after heating showed in the same time no effect.

As far as these experiments go they indicate that there is a slow change in thermoluminescent salts, probably similar to that occurring at the higher temperature, and that the total change depends on the original intensity, the time and the nature of the salt.

New Series in the Spectra of Ca, Sr and Ba.<sup>1</sup> By F. A. Saunders.

PHOTOGRAPHS with a quartz spectrograph show a new series of lines in the arc spectrum of Ca whose approximate wave-lengths are 2399, 2276, 2201, 2151, 2118, 2098, 2084, 2073. A similar series is present in Sr, also at  $\lambda$  2428, 2354, 2309, 2277, 2254, 2239, 2228. In Ba the following lines seem to form the beginning of a similar series, though it fades off very rapidly: 3071, 2597, 2380. The Ca and Sr series are well represented by formulæ only slightly modified from the Ritz type, involving four constants, but no suitable 3-constant formula has been found for them.

The series of pairs in the Sr and Ba spectra whose existence was first announced by Rydberg from the Zeeman effect, and whose formulæ are given by Ritz² calculated from the first two members of each subordinate series and the first principal series member, have been extended by the additions of the following new pairs:

```
Sr. 1st subordinate series, 1/\lambda = 50122 and 50900 2d subordinate series, 1/\lambda = 48717 and 49508 Ba. 1st subordinate series, 1/\lambda = 44719.1 and 48676 46410.4 46410.4 46410.4 2d subordinate series, 1/\lambda = 43727.5 and 48027 45418.6 and 48027
```

A three-constant formula of the Rydberg type suitably represents these series, as enlarged, but the one given by Ritz fails to do so.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

<sup>&</sup>lt;sup>2</sup> Phys. Zeitschr., 9,521, 1908.

### THE

## PHYSICAL REVIEW.

### CRYSTAL RECTIFIERS FOR ELECTRIC CURRENTS AND ELECTRIC OSCILLATIONS.

PART II. CARBORUNDUM, MOLYBDENITE, ANATASE, BROOKITE.

By George W. Pierce.

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### INTRODUCTION.

Concerning Part I. - Carborundum had been found by General Dunwoody 1 to be capable of acting as a receiver for the electric waves of wireless telegraphy. Having learned of this property of carborundum, the writer thought that a further study of the electrical behavior of this substance would be interesting. In the course of this study, an account of which has been published in the PHYSICAL REVIEW<sup>2</sup> for July, 1907, it was discovered that when a piece of carborundum is placed in a clamp between contact electrodes, the hetereogeneous conductor consisting of the carborundum and the electrodes permits the passage of a greater current in one direction than in the reverse direction under the same applied voltage. The device can be used as a rectifier for small alternating currents and oscillations. The phenomenon is very striking. example, with one specimen under an electromotive force of 30 volts the current in one direction is 4,000 times as great as the current in the opposite direction under the same external voltage.

Although the rectified current is not large (in the case just cited, 3 milliamperes in one direction and .00075 milliampere in the opposite direction) such a rectifier, being constructed entirely of solid parts, possesses sufficient permanence and constancy to permit of many useful applications, where the detection and measurement of small alternating currents is required. As an example of such applications details are given in Part I. of the employment of the rectifier in the construction of an alternating current voltmeter operable with an extremely small consumption of energy.<sup>3</sup>

Questions Arising in Connection with the Phenomenon. — Many questions of theoretical interest arise in connection with the phenomenon. Is the action localized at the surface of contact between the crystal and the metallic electrode? Is the action due to electrolytic polarization? Is the action thermoelectric, conditioned on unequal heating of the two electrode contacts? If the phenomenon is novel, how is it related to the hitherto studied properties of conductors?

In the experiments on carborundum performed by the writer the

<sup>&</sup>lt;sup>1</sup>Dunwoody, U. S. Patent, No. 837,616, issued December 4, 1906.

<sup>&</sup>lt;sup>2</sup> Pierce, Phys. Rev., Vol. 25, pp. 31-60, 1907.

<sup>&</sup>lt;sup>8</sup>G. W. Pierce, U. S. Patent, No 879,061.

investigation of these questions met with limitations on account of the occurrence of the carborundum in discrete masses to which electrodes could not be rigidly attached; so that the conditions at the electrodes could not be widely varied. However, by increasing the pressure of the electrodes against the carborundum beyond a certain limit, and by cathodically platinizing the surfaces of the carborundum at both the contact areas, the rectification though not entirely eliminated was rendered very imperfect; that is to say, the ratio of the strength of the current in one direction to that in the reverse direction approached unity. On the other hand, platinizing one only of the surfaces of contact, while the other surface was left unplatinized, generally rendered the rectification more nearly perfect. This fact indicated that the seat of the action was the area of contact with the electrodes, and that the action at the two contacts were in opposition to each other, so that when the action at one of the contacts was reduced by platinizing, the rectification at the other contact appeared more pronounced.

These characteristics of the phenomenon are consistent with the view that the rectification is conditioned on the localization of the energy of the circuit at the high resistance boundary between the two different classes of conductors, the crystal and the metallic electrode.

Now such a localization of energy at the boundary of the two conductors is favorable to the production of electrolytic polarization, if we may have electrolytic polarization in solids, and is also favorable to the production of a thermoelectromotive force, either of which might result in rectification.

Nevertheless, in Part I., a number of experiments are described which were taken to indicate that neither electrolysis nor thermoelectricity plays an important part in the phenomenon.

On the Question of Electrolysis, the following experiment, performed since the publication of Part I., has a bearing.

Experiment Showing Permanence of the Carborundum Rectifier.

— In confirmation of the absence of electrolytic polarization, a durability test of the rectifier has later been made as follows: A crystal of carborundum enclosed in a glass tube with a few drops of oil 1 and held between brass electrodes, one of which was under

<sup>1</sup> The oil was put in to prevent accumulation of moisture.

tension of a spiral spring, was kept under almost daily observation 1 from October 23, 1907, until March 18, 1908. During this time more than 1.200 measurements were made of the direct current obtained through the crystal under different direct and alternating voltages. The rectifier was kept in a thermostat and subjected to various long periods of heating and cooling ranging from 0° to 80° C. Notwithstanding the long continued exposure of the crystal to large changes of temperature, and notwithstanding the frequent loading and occasional overloading of the rectifier with current, it was found at the end of the series that the values of the direct current obtained trom the crystal under a given applied alternating voltage over a range of current from 4 to 400 microamperes (direct) and a range of voltage between 1.5 and 6 volts (alternating) did not differ from the corresponding values at the beginning of the series by an amount exceeding the limit of accuracy of the experiment, which was about one third of I per cent.

This experiment shows that if there is any kind of electrolytic action, it must be of such a character as not to change the nature of the electrodes or of the crystal.

On the Question of a Possible Thermoelectric Origin of the Phenomenon. — It is apparent that the disposition of the carborundum for the best rectification is exactly the most favorable disposition for the development of a thermoelectric voltage at the high resistance contact. This voltage, being always in one direction, by superposition on an alternating current through the crystal, might give rise to a unilateral cycle through the crystal. In Part I., several experiments are described which present evidence adverse to this explanation, and the opinion is expressed that "heat is practically a negligible factor in the process."

However, since it is very important to exclude the possibility of bringing the experiments into consistent relation with thermoelectricity before admitting that we are dealing with a new phenomenon, the question of the applicability of the thermoelectric explanation is taken up anew in the present account.

<sup>&</sup>lt;sup>1</sup> This series of measurements were carried out by Mr. K. S. Johnson, to whom the writer wishes to express his sincere thanks. The experiment was finally discontinued on account of the accidental melting of the cement holding in the ends of the tube.

Extension of the Experiments to Other Crystals. — Prior to the publication of Part I., the writer had found a number of other crystals showing the rectifying property similar to carborundum. These have now been under investigation for a period of more than a year, and though the work is by no means completed, it is thought that an account of the experiments as far as they have gone may be of interest. The present account deals with the rectifying action of anatase, brookite and molybdenite in contact with a metallic electrode.

### ANATASE AND BROOKITE.

Anatase. — Anatase, an octahedral crystal of oxide of titanium with the chemical formula TiO<sub>2</sub>, was found to rectify quite markedly when placed in a clamp, under a contact pressure of I to 3 kilograms. Current-voltage curves <sup>1</sup> of anatase, with a diagram of the disposition of the crystal in the experiment, are given in Fig. I. The

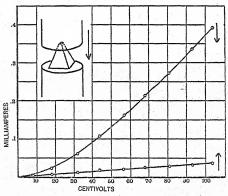


Fig. 1. — Current-voltage curves for anatase, with direct current.

upper curve was obtained when the current was through the crystal in one direction, the lower curve was with the current in the opposite direction, as indicated by the arrows. The contact pressure in this experiment was 2 kilograms. These curves have the same general form as those obtained in the experiments on carborundum. By a

<sup>1</sup> The current-voltage curves were drawn in Part I. with positive coördinates when the current was in one direction and negative coördinates when the current was in the opposite direction. In order to economize space in the present account, both the positive and negative currents are drawn in the same coördinate quadrant. This has the advantage of permitting an easier comparison.

comparison with Part I., it is seen, however, that the anatase gives much larger currents with a small applied voltage than does the carborundum. This characterizes the anatase as a much more sensitive rectifier for small alternating voltages and as a much more sensitive detector for electric waves than is the carborundum.

Brookite. — This is another crystal form of TiO<sub>2</sub>, which was found to serve as a rectifier of small alternating currents with about the same sensitiveness as anatase. Although a considerable amount of time was spent in experimenting with anatase and brookite, these substances, occurring, like carborundum, in discrete pieces to which terminals could not be attached, did not serve to throw much light on the phenomenon. Numerical data in regard to them are, therefore, omitted.

### MOLYBDENITE.

One of the most sensitive and interesting of the rectifiers thus far investigated makes use of molybdenite as a member. Molybdenite, with the chemical formula MoS<sub>2</sub>, is a mineral occurring in nature in the form of tabular hexagonal prisms with eminent cleavage parallel to the base of the prism. The cleavage of the crystal resembles that of mica, and thin sheets of the mineral several square centimeters in area may be scaled off from a large crystal of molybdenite. These sheets have a metallic lustre and look not unlike sheets of lead foil. They can be readily electroplated with copper, so that connecting wires may be soldered to them. This property, together with the thinness of the sheets and the ease with which the thermoelectric property of the substance may be studied, admirably adapts it to the present experiments.

The Molybdenite Rectifier. — The rectifying action of the molybdenite was first obtained with a thin, flat specimen of the mineral held between flat contact electrodes in a clamp of which the two jaws were insulated from one another. With this form of mounting the molybdenite also acts as a receiver for electric waves with or without a battery in the local circuit.

It was soon found, however, that the apparatus was more sensitive

<sup>&</sup>lt;sup>1</sup> See also G. W. Pierce, "A Simple Method of Measuring the Intensity of Sound," Proc. Am. Acad., Vol. 43, p. 377, February, 1908, in which the molybdenite rectifier was employed.

as a receiver for electric waves and as a rectifier, when one of the contacts between the molybdenite and the electrode had a high resistance. A form of mounting in which this is attained is shown in section in Fig. 2. T is a threaded brass post on the top of which

is placed a disc of mica N. On top of the mica is a thin circular disc of the molybdenite M with an area of about I square centimeter, leaving a projection of the mica beyond the periphery of the molybdenite. A hollow cap D, threaded inside and having a conical hole at the top, is screwed down on the post T so as to clamp the molybdenite between the mica disc  $^1$  and the annular shoulder of the cap, with the upper surface of the molybdenite exposed above. At the free surface of the molybdenite contact is made with metallic rod P.

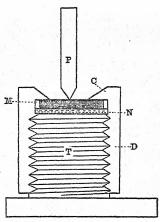


Fig. 2. Holder for molybdenite.

The rod P was either supported unadjustibly as in the author's experiments on sound,<sup>3</sup> or it was mounted in a manner to permit of ready adjustment as is shown in Fig. 3. The clamp K containing the molybdenite is metallically connected with the binding post H (Fig. 3). Another binding post is attached to the metallic block A, on top of which is supported a stout spring B. Through a hole in B provided with a set screw, the rod P is allowed to drop down into contact with K. The set screw is then tightened against P, and the final adjustment is made by the slow-motion screw S. The apparatus is connected in circuit by means of the binding posts, so

¹ The purpose of the mica disc under the molybdenite is to confine the current as much as possible to the upper layer of the molybdenite. This was done so as not to complicate the phenomenon by conduction across the laminæ of the substance, and also so that when the detector is immersed in oil in some of the later experiments, the oil shall have free play over the conducting surface and over the contacts, and serve the better to avoid possible changes of temperature of the essential parts of the apparatus.

 $^2$  In the diagrams of Fig. 2 and Fig. 3, the lower end of the rod P is shown pointed. It is found, however, that the end of the rod P may be blunt or even flat with an area as great as 4 sq. mm. without much loss of sensitiveness of the instrument as a receiver for electric waves or as a rectifier.

<sup>3</sup> Loc. cit.

that the current of the circuit is made to enter the molybdenite through the contact area between P and the molybdenite and to leave by way of the contact between the molybdenite and the cap C, or the reverse. It is found that a larger current flows in one direction

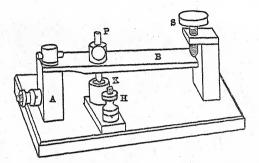


Fig. 3. Mounting of molybden te.

than in the reverse direction for a given applied elecromotive force.

Current-voltage Characteristic of the Molybdenite Rectifier. - A large number of current-voltage curves of the molybdenite rectifier with the form of mounting shown in Fig. 3, have been taken both with direct and alternating applied voltages. Two sets of these curves, with the corresponding tables are here given. In taking the observations of Fig. 4, Table I., the rectifier was submerged in a constant temperature oil-bath. The oil was rapidly stirred and had free access to the surface of the molybdenite and to the point contact between the molybdenite and the copper rod. A steady voltage was applied to the terminals of the rectifier, and the current through the crystal was measured. The voltage was then reversed and the current again measured. The process was repeated with various values of the voltage. These values thus obtained in the oil-bath were found to be the same as the corresponding values when the rectifier was in air at the same temperature. That is, the presence of the oil about the rectifying contact did not materially affect the process.

The values of Table I. are plotted in the curves A and B of Fig. 4. A is the curve obtained when the current was sent from the copper to the molybdenite, B the corresponding curve when the current was sent from the molybdenite to the copper. These curves

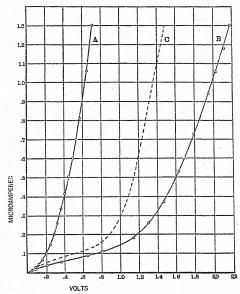


Fig. 4. Current-voltage curves of the molybdenite rectifier. A, current from copper to molybdenite; B, current from molybdenite to copper; C, excess voltage.

TABLE I.

Current-Voltage Values for the Molybdenite Rectifier.

Current from Co	pper to Molybdenite.	Current from Mo	olybdenite to Copper.
Volts.	Microamperes.	Volts.	Microamperes
.0407	.012	.082	.020
.0815	.025	.203	.038
.122	.043	.363	.058
.163	.068	.651	.090
.203	.102	.815	.114
.244	.147	1.140	.185
.285	.202	1.300	.261
.326	.262	1.465	.375
.363	.337	1.630	.534
.407	.415	1.79	.732
.447	.504	1.96	.947
.488	.600	2.03	1.056
.529	.700	2.12	1.180
.570	.812	2.18	1.306
.651	1.062		
.710	1.306		1

resemble those obtained in Part I with carborundum. The molybdenite rectifier is, however, seen to operate with a much smaller resistance than the carborundum rectifier. This makes the molybdenite rectifier applicable to use with smaller voltages than the carborundum, consequently the molybdenite rectifier is a more sensitive detector for electric waves or for small alternating voltages than the carborundum rectifier. In fact, the molybdenite rectifier, with selected specimens of molybdenite, when used as a detector for electric waves, is, so far as the writer can judge, equal in sensitiveness with the most sensitive detectors heretofore employed in wireless telegraphy. Also the molybdenite rectifier, giving comparative large values of direct current for small values of applied alternating voltage, affords a sensitive method of measuring the small alternating voltages arising in telephony and in experiments on sound. Application of the rectifier to the measurement of sound has been made in a paper entitled a "Simple Method of Measuring the Intensity of Sound."1

Referring again to Fig. 4, attention is called to the dotted curve C. This curve is calculated from the curves A and B by subtraction of corresponding abscissas. The curve C, therefore, represents the excess of voltage required to force the current from the molybdenite to the copper above that required to send an equal current in the opposite direction. The table of values for curve C follows as Table II.

TABLE II.

Excess of Voltage to Send Current from MoS<sub>2</sub> to Cu above that to Send

Current from Cu to MoS<sub>2</sub>.

Microamperes.	Excess Volts.	Microamperes.	Excess Volts.
.05	.18	.70	1.24
.10	.515	.80	1.27
.20	.89	.90	1.32
.30	1.01	1.00	1.36
.40	1.09	1.10	1.40
.50	1.15	1.20	1.45
.60	1.19	1.30	1.48

The current-voltage values for the molybdenite rectifier differ for different specimens and for different adjustments of the same speci-

<sup>&</sup>lt;sup>1</sup> Pierce, Proc. Am. Acad., Vol. 43, p. 377, February, 1908.

men. The results of another experiment, in which larger values of the current and voltage are employed, are given in Table III. These values were obtained with a specimen mounted somewhat differently from the mounting in Fig. 3, in that, in order to eliminate any possible uncertainty from the use of the clamp holder K (Fig. 3), the tight-contact terminal was soldered to a copper plated area on the molybdenite, and the sheet of molybdenite with its soldered terminal were held down upon a block of wood by means of a mica covering screwed to the block. A hole through the mica covering admitted the contact rod P.

TABLE III.

Current-Voltage Values for the Molybdenite Rectifier. Larger Currents.

Current from Copper to Molybdenite.		Current from Mo	lybdenite to Copper.	
Volts.	Milliamperes.	Volts.	Milliamperes.	
.5	.20	2.0	.02	
.6	.50	4.5	.10	
.77	1.00	5.27	.25	
.84	1.50	7.1	.55	
.92	2.00	8.6	1.15	
1.07	2.50	10.1	2.20	
1.15	3.00			
1.32	4.00		10.0	
1.52	5.00			
1.70	6.00			
1.88	7.00			
2.00	8.00			
2.15	9.00			
2.22	10.00			

The values recorded in Table III. are plotted in Fig. 5. By a reference to the curves or to the table it is seen that the rectification at 10 milliamperes is practically perfect; the current from the molybdenite at 2.2 volts is 10 milliamperes, while the current in the opposite direction at the same voltage is about .02 milliampere. This is a larger value of the rectified current, at practically perfect rectification, than I was able to obtain with the carborundum rectifier. It was, therefore, decided to recur to the attempt to obtain an oscillographic record of the phenomenon, as had been attempted

with only partial success in the study of carborundum. The result in the present experiment is highly satisfactory.

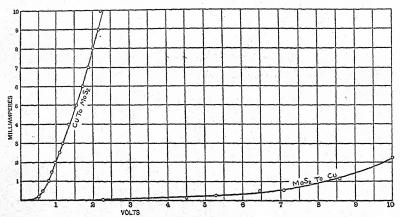


Fig. 5. Current-vocaltage rves of molybdenite recitfier, with large current.

### OSCILLOGRAPHIC RECORDS OF RECTIFIED CYCLE.

Method of Obtaining the Oscillograms.—After a prolonged attempt to use an Einthoven galvanometer, which was found to be impracticable on account of the natural period of the "string" of the galvanometer, the Braun's tube oscillograph was employed A sketch of the oscillographic apparatus is given in Fig. 6. The

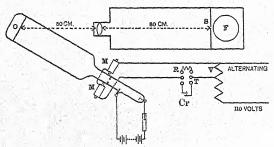


Fig. 6. Oscillographic apparatus.

Braun's tube was filled with hydrogen and was pumped to the vacuum at which it has its highest sensitiveness.¹ The high-potential current through the tube was supplied by Professor Trowbridge's

<sup>&</sup>lt;sup>1</sup> My thanks are due to Mr. E. L. Chaffee for very carefully pumping out the tube for me, and for other valuable assistance with the oscillographs.

40,000-volt storage battery, which he kindly placed at my disposal. Usually only 20,000 volts of the battery were employed, and this was controlled by means of a running-water rheostat in series with the battery and the tube.

The cathode beam in the tube produced a luminescent spot on the fluorescent screen at O. The electromagnets, through which the current to be oscillographed was sent, were placed above and below the Braun's tube at MM. Therefore, the deflection of the spot was in a horizontal line perpendicular to the plane of the figure. The photograph of the moving luminescent spot was taken on a sheet of bromide paper carried by a rotating drum F, which made 20 revolutions per second about a horizontal axis. This drum was enclosed in a light-tight box at the back of an improvised camera. A horizontal slit S, immediately in front of the rotating drum, shut off all luminescence in the tube except that in the line of motion of the spot.

The rotating drum was driven by a synchronous motor operating on the 60-cycle alternating current mains of the laboratory. The alternating current sent through the rectifier and the deflecting magnets was taken from the same supply. The synchronism of the drum with the deflections of the luminescent spot was so perfect that exposures of four minutes could be made, during which time the image of the spot moved over the sensitive paper 4,800 times, without any failure of perfect superposition, and without any appreciable fogging of the paper.

The deflecting electromagnets MM had a combined resistance of 436 ohms, and were provided with soft iron cores about 6 millimeters in diameter. With these deflecting coils a direct current of 1.5 milliamperes gave a deflection of 1 cm. on a ground glass put in the place of the sensitive paper at the back of the camera. A calibration for different values of direct current through the coils showed the deflections of the light spot to be proportional to the current, and for the small values of current employed showed no evidence of hysteresis in the iron.

The Oscillographic Records. — Reproductions (reduced to  $\frac{1}{3}$ ) of a characteristic set of the oscillographic records obtained are given in Plate I. Oscillograph No. 1 was taken with the molybdenite rectifier adjusted to give practically perfect rectification. No. 2 is with the

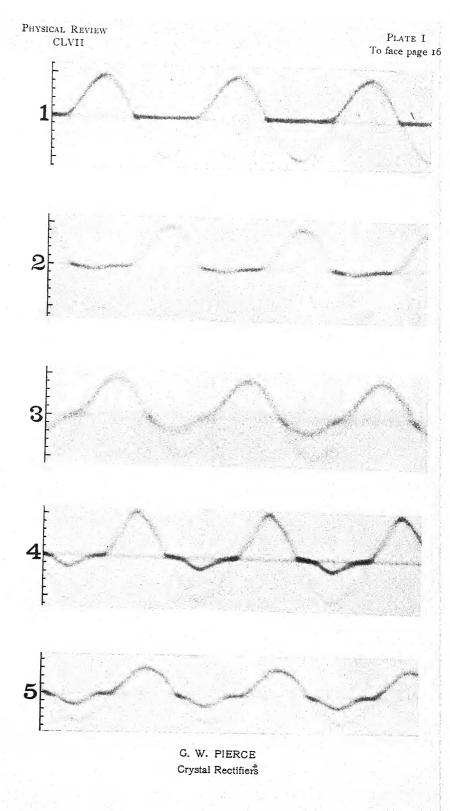
same rectifier slightly out of adjustment (overloaded), so that the rectification is less perfect. No. 3 is with the same rectifier further out of adjustment. No. 4 is an oscillographic record with the carborundum rectifier. No. 5 is with the rectifier of brookite. In taking No. 2, the rectifier was submerged in oil, to test the effect of cooling, which was found to have no effect.

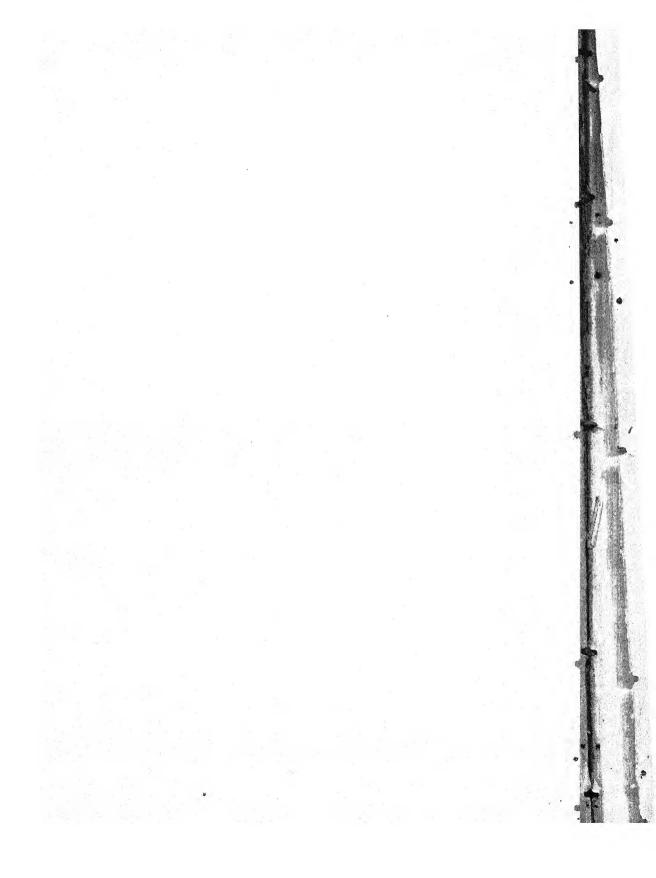
In making these records the following steps were taken: The drum carrying the film was set rotating. The high-potential current was started in the tube. The potential V(Fig. 6) and the contact of the rectifier were adjusted so that the deflection of the luminescent spot on the fluorescent screen was wholly or chiefly to one side of the zero position. Exposure of about 2 minutes was then made. This exposure gave the heavy line of the oscillograms. The switch at T was then thrown open, so that the luminescent spot came to its zero position. The exposure in this position was made for a shorter time of about 40 seconds. This traced the light straight line along the center of the picture, and gave the axis of zero current. The switch T was then thrown to the position to put the resistance R in the circuit in place of the crystal. The resistance R had been previously adjusted so that the amplitude of the deflection with R in the circuit should coincide with the amplitude with the crystal in the circuit. With the resistance R in circuit an exposure of about one minute was made, giving the light sinusoidacurve of the picture.

On each picture the three exposures give, therefore, (1) the form of the rectified cycle as a heavy line, (2) the position of the axis of zero current, as a straight line through the figure, and (3) the form and position of the alternating-current cycle when an equivalent resistance R is substituted for the rectifier. The last-named cycle appears in the pictures as a thin-lined sine curve. This curve is in phase with the impressed voltage immediately about the crystal, and is referred to below as the "voltage-phase curve."

In tracing all the curves, the motion of the light spot over the paper is from left to right; the time coordinate is, therefore, the abscissa of the curves and is drawn as usual from left to right.

The scale drawn in ink at the left-hand margin of each picture gives the value of the current; one division being one milliampere.





A tabular description of the conditions under which each of the records was taken is contained in Table IV.

TABLE IV.

Tabular Description of the Oscillographic Records of Plate I.

No.	Material of Rectifier.	Condition.	Maximum Rectified Current in Milli- amperes.	R.M.S. Alternating Volts.	Equivalent Resistance in Ohms.
1	Molybdenite.	Good adjustment.	4.9	3.54	400
2	46	Out of best adjustment.	4.9	3.54	400
		Submerged in oil			
1		and overloaded.	1.0	1.0	
3	"	Out of best adjustment.	4.5		1 11 -
		Overloaded.		4	
4	Carborundum, platin- ized on one side.	Overloaded.	5.4	22.0	6000
5	Brookite	"	3.0	2.22	992

A discussion of the records follows.

Oscillograms 1, 2 and 3, Molybdenite.—The pressure of the copper rod¹ against the molybdenite for good rectification is slight, and is somewhat difficult to attain. Some points of the crystal are more sensitive than others, and the crystal has to be moved around under the copper contact and tried at several different points before the best adjustment can be found. Oscillogram No. 1, Plate I., was taken with a molybdenite rectifier in good adjustment. The rectification in this case is seen to be practically perfect; the cycle through the specimen consists of a nearly sinusoidal curve for one half-period and a practically straight line for the other half-period. The large current flows from the copper to the molybdenite, and the zero current from the molybdenite to the copper.

When the pressure on the contact was increased until a smal negative current was permitted to pass, oscillogram No. 2 was obtained. Increasing the pressure still more so as to get a larger negative current gave oscillogram No. 3.

One object in taking these oscillograms, together with the voltage-phase cycle, was to see if there is any evidence of lag of the rectified cycle with respect to the voltage-phase cycle. No such

<sup>&</sup>lt;sup>1</sup> The end of the copper rod in contact with the molybdenite had an area of 4 sq. mm.

lag appears. On the other hand, the rectified cycles lead their respective voltage-phase cycles at three positions:

The first of these positions of lead is at the part of the cycle in which the rectified current approaches the zero axis after having traversed the upper half of the curve. This advance, which is so small as to be just perceptible in the oscillograms, amounts to about 1/6000 of a second.

A second, somewhat larger, lead of the rectified cycle ahead of the voltage-phase cycle is at the point of rising from the axis after the rectified current has followed for a half period along the zero axis. The lead here is about 1/1500 of a second.

A third, very significant, lead of the rectified cycle is at the negative maximum, as is seen in the cases of imperfect rectification, oscillograms 2 and 3. Here the lead is a large fraction of a half period.

Oscillogram No. 4, Carborundum. — Oscillogram No. 4, Plate I., was obtained with a carborundum rectifier consisting of a specimen of carborundum, platinized on one side, and held in a clamp under a contact pressure of 3 kg. When sufficient current was sent through the carborundum to give deflections suitable for the oscillogram, the carborundum was overloaded, and permitted current to pass in the negative direction. The carborundum cycle differs from the molybdenite cycle in the absence of lead at the negative maximum and at the point of rising from the zero axis. This anomaly in the case of the carborundum rectifier is seen later to be the effect of its high resistance.

Oscillogram No. 5, Brookite. — The form of the cycle obtained in this case is intermediate between the carborundum cycle and the cycle of oscillogram No. 3. This is consistent with the value of its resistance.

In order to investigate the meaning of the lead of the rectified cycles in the several cases a further examination of the oscillograms is made with the aid of the theory of alternating currents.

Examination of the Oscillograms with the Aid of the Theory of Alternating Currents.

The so-called "voltage-phase cycle" gives the instantaneous values of the current through the deflecting coils and a resistance

chosen to make the amplitude of this current the same as the amplitude of one loop of the current through the rectifier, under the same applied voltage. Although the current of the voltage-phase cycle lags behind the externally applied voltage by an amount depending on the relation of the self-inductance of the deflecting coils to the resistance of the circuit, the current is nevertheless in phase with the voltage immediately about the substituted resistance; for the voltage about a resistance is in phase with the current through it. by throwing the switch T of Fig. 6 we put the rectifier in the circuit in the place of the resistance. If the rectifier, when current traverses it, introduces into the circuit electromotive forces out of phase with the current through it, we ought to get a shift of phase of the cycle. We can easily see, for example, that if the rectifier contained capacity or inductance, such a shift would occur. Also, if the action of the rectifier were one of electrolytic polarization, the back E.M.F. of polarization would be approximately determined at any part of the cycle by a time integral of the current, and would introduce a shift of phase resembling that introduced by a capacity.<sup>1</sup>

Also, if the action of the rectifier were due to thermoelectricity, we should expect the thermal electromotive forces developed to be of the form

$$(1) \pm a \int i^2 r dt$$

due to the Joulean heat at the high resistance, and of the form

$$(2) \pm b \int idt$$

due to the Peltier effect at the junctions. To these terms we should have to add also terms taking account of conduction of heat from the junctions. The term for the conduction of heat would be difficult to assign definite values, but they would be functions of the rise of temperature of the junctions, and may be written in the general form

(3) 
$$F(\int i^2 r dt, \int i dt)$$
.

The terms (1), (2) and (3), when put into the differential equation for the current through the circuit and integrated (if possible), would

<sup>&</sup>lt;sup>1</sup> B. O. Pierce, Newtonian Potential Function, p. 323, Boston, 1902.

give in the result a shift of phase of the current with respect to the voltage-phase cycle.

Let us, therefore, attempt to determine whether there are any phase differences between the rectified cycle and the voltage-phase cycle that are not accounted for by the conditions existing in the oscillographic apparatus. In doing this we shall make use of the current-voltage characteristic of the molybdenite rectifier, as obtained with the current and voltage in the steady state, and recorded in Table III. and Fig. 5. This table of data was obtained with the same molybdenite rectifier in practically the same adjustment as in the oscillograms I and 2 of Plate I.

Let us derive first the numerical equation for the "voltage-phase" curve. In the case of oscillogram No. 1, an ohmic resistance of 400 ohms was in series with the deflecting coils, which had a resistance of 436 ohms, making a total resistance of 836 ohms. Let the inductance of the coils be L. The value of L can be calculated from the voltage and current of the cycle. The R.M.S. voltage impressed on the circuit was 3.54 volts; the maximum voltage was therefore 5.00 volts. The maximum current taken from oscillogram No. 1 was  $4.9 \times 10^{-3}$  amperes, whence we have

$$4.9 \times 10^{-3} = \frac{5.0}{\sqrt{836^2 + L^2 \omega^2}}.$$

Therefore

$$L\omega = 584,$$

(2) 
$$\tan^{-1} \frac{L\omega}{836} = \varphi_1 = 35^{\circ},$$

and the equation for the current  $i_1$  of the voltage-phase cycle becomes

(3) 
$$i_1 = \frac{5.0}{\sqrt{836^2 + 584^2}} \sin(\omega t - 35^\circ).$$

From this equation the values obtained in Table V. were computed, and from these values three half-periods of the voltage-phase cycle are plotted as the sinusoidal curve S of Fig. 7.

The computations when the rectifier is put in place of the 400

TABLE V.

The Voltage-Phase Cycle.

Degrees.		Current in Milliamperes.	ω <i>t</i> Degrees.	Current in Milliamperes.	
-	. 35	0	135	4.82	
	55	1.67	155	4.23	
	75	3.14	175	3.14	
	95	4.23	195	1.67	
	-115	4.82	215	0	
	125	4.90			

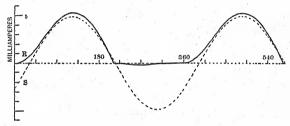


Fig. 7. Rectified cycle computed from the current-voltage values of Fig. 5.

ohm resistance can be made only approximately. The differential equation for the current  $i_2$  through the circuit in this case is

(4) 
$$E \sin \omega t - e_r = R_c i_2 + L \frac{di_2}{dt},$$

in which  $e_r$  is the drop of voltage about the rectifier, E is 5.0 volts, and  $R_o$  the resistance of the deflecting coils = 436 ohms. The drop in voltage  $e_r$  about the rectifier is a function of the current. This function is the equation of the current-voltage curve of Fig. 5. It is difficult to obtain an exact analytical expression for this function. But for values of current between I and 6 milliamperes, when the current is from copper to molybdenite,  $e_r$  is approximately a linear function of the current, with the equation

(5) 
$$e_r = q + ri$$
, in which  $q = .60$  volt,  $r = 183$  ohms.

With this approximation, equation (4) becomes

(6) 
$$E \sin \omega t - q = (r + R_o)i_2 + L\frac{di_2}{dt}$$

Integration of this equation gives

(7) 
$$i_{2} = \frac{E}{\sqrt{(r+R_{o})^{2} + L^{2}\omega^{2}}} \sin\left(\omega t - \tan^{-1}\frac{L\omega}{r+R_{c}}\right) + ce^{-\frac{(R_{c}+r)t}{L}} - \frac{q}{R_{c}+r},$$

in which c is a constant of integration. If we substitute known values in this equation; namely,

(8) 
$$r + R_c = 183 + 436 = 619,$$

$$L\omega = 584,$$

$$E = 5.0,$$

$$q = .60,$$

we have

(9) 
$$i_2 = 5.87 \times 10^{-3} \sin(\omega t - 43^{\circ}.3) + ce^{-1.06\omega t} - .97 \times 10^{-3}$$
.

For the determination of the constant c we have the relation  $i_2 = 0$  when  $E \sin \omega t = q$ . This gives c = 5.1.

From equation (9), values for the current in the upper loop of the rectified cycle for various values of  $\omega t$  were computed, and are given in Table VI.

TABLE VI.

Computed Values of the Rectified Cycle. Upper Loop.

ωź Degrees.	Current in Milliamperes.	ωt Degrees.	Current in Milliamperes.
0	0	130	5.26
20	.32	140	5.20
40	1.17	160	4.50
60	2.45	180	3.15
80	3.61	200	1.40
100	4.75	213	0
120	5.21		

The lower loop of the rectified cycle was obtained in a similar manner. In this case the drop in potential about the rectifier was obtained from the curve of current from molybdenite to copper of Fig. 5. The equation to this curve, within the limits employed in the calculations, is approximately

(10)  $e_r = q_1 + r_1 i_3$ , in which  $q_1 = 3.8$  volts, and  $r_1 = 6470$  ohms.

These values substituted in an equation of the form of equation (7) give, since the exponential term was found to be negligible,

(II) 
$$-i_3 = .72 \times 10^{-3} \sin(\omega t - 4.8) - .55 \times 10^{-3}$$
.

Computations from this equation give the values of current recorded in Table VII.

TABLE VII.

Computed Values of the Rectified Cycle. Lower Loop.

ωt Degrees.	Current in Milliamperes.	Degrees.	Current in Milliamperes.
220	0.00	280	.16
240	.07	300	.07
260	.16	320	.00
270	.17		- 1

The computed values of Tables VI. and VII. are plotted as the continuous curve R of Fig. 7, along with the voltage-phase curve which is the dotted sine curve S.

The data used in the computations are entirely independent of the oscillograms, except that the amplitude of the voltage-phase cycle was taken from oscillogram No. 1 or No. 2, and this value was used in determining the self-inductance of the circuit.

The agreement of the diagram of Fig. 7 with the oscillograms No. I and 2 of Plate I. is very striking, as regards both the form and the absolute value of the curves. The agreement with oscillogram No. 2 is a little better than with No. I, and is within the limit of error of the measurement of the photograph. No departure in amplitude or in phase exists between the rectified cycle and the voltage-phase cycle that is not accounted for by the inductance and resistance of the oscillographic apparatus or by the current-voltage curves of the rectifier with steady currents.

This means that if there are any terms, contingent upon heating or other effects which involves an intergal of a function of the current with respect to the time, this integral attains its final value in a time within the limit of error of measuring the oscillograms, which is about 1/6000 second. This time corresponds to 3.5°, and is about 1 mm. on the original photographs.

It might seem that the approximation made as to the analytical expression for the steady current-voltage curve would not warrant the accuracy here claimed; but if we draw the straight line through the points for which the current is I and 6 milliamperes, this line will depart from the observed values only for values of i below I milliampere, where the departure will have the following values:

i	Departure.	Departure in
Millamperes.	Volts.	Degrees.
.5	.1	.6
.2	.15	1.7
.1	.3	3.4

In the negative loop of the rectified cycle the departure of the approximation from the observed current-voltage curve is still smaller. However, apart from the specific assumption as to the analytical function representing the current-voltage characteristic of the rectifier under the action of a steady current, the theoretical discussion given above permits a ready qualitative understanding of the lead that occurs in certain parts of the rectified cycle, which may be summarized as follows:

- I. The case of the advance of the rectified cycle on rising from the axis of no current is seen to be due largely to the fact that after a dormant half-period the current in the circuit follows the ordinary exponential "building-up" curve for a time before coming into coincidence with the sine curve. This building-up curve starts from the axis with zero lag and is, therefore, in advance of the sine curve. To this effect is to be added the effect due to an apparently higher resistance of the rectifier for small currents than for large currents. This apparently higher resistance brings the building-up curve a little nearer to the sine curve.
- 2. The slightly quicker descent of the rectified cycle on approaching the axis after having traversed the upper half of the curve is also due to this apparently higher resistance of the rectifier when traversed by smaller currents.
- 3. The very significant lead of the negative maximum ahead of the corresponding voltage-phase maximum is explicable on the assumption that the rectifier has a much higher resistance in the negative direction than in the positive direction. We have seen above that the angle of lag of the voltage-phase cycle behind the impressed

voltage, determined by the inductance and resistance of the circuit, is

$$\tan^{-1}\frac{584}{836} = 35^{\circ}$$
,

while in the negative direction in order to bring the voltage-phase curve to the same amplitude as the negative maximum of the rectified cycle there would be required a resistance of at least 6,470 plus 436 = 6,906 ohms, whence the angle of lag in this case would be

$$\tan^{-1} \frac{584}{6906} = 4.8^{\circ}$$
.

Therefore the angle of lead of the rectified cycle ahead of the voltage-phase cycle, determined as the difference of these two angles of lag, is 30.2°. This value agrees with oscillogram No. 2.

In this connection it is interesting to notice that a lead of this negative maximum in the case of the carborundum oscillogram does not appear. The explanation of this is easily obtained if one substitutes for the resistance values of the molybdenite the corresponding values for the circuit containing the carborundum rectifier. The equivalent resistance of the carborundum in its positive loop is 6,000 ohms, so that the angle of lag of the voltage-phase cycle with this resistance in it is only 5.6°, while in the negative direction the equivalent resistance of the carborundum is about 20,000 ohms, giving an angle of lag in the neighborhood of 1°. The difference between these two angles of lag, which would give the phase difference between the carborundum cycle and the corresponding voltage-phase cycle would be a quantity just perceptible on the oscillogram, as was verified in the original protographs.

In conclusion of this discussion of the oscillograms, I should say that we have not been able to detect in the photographs any evidence of a thermoelectric or other integrative action of the rectifier.

### THERMOELECTRIC PROPERTIES OF MOLYBDENITE.

In the present section an account is given of the investigation of the thermoelectromotive force of molybdenite against copper, and a determination of the temperature coefficient of resistance of molybdenite. Apart from their possible bearing on the action of the rectifier, these properties of molybdenite are of interest in themselves.

Thermoelectromotive Force. — Five specimens were mounted for

the study of the thermoelectromotive force of molybdenite against copper. These specimens are referred to as A, B, C, D, E. The method of mounting the specimen E is shown in

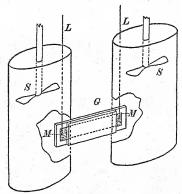


Fig. 8. Apparatus for determining thermoelectromotive force of molybdenite against copper.

Fig. 8. A thin sheet of molybdenite .1 or .2 mm. thick, 2 cm. wide, and 8 cm. long, was cemented between two glass microscope

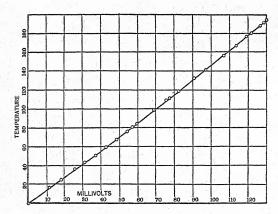


Fig. 9. Thermoelectromotive force of copper-molybdenite couple *E* for various  $\frac{1}{2}$  temperatures of hot junction. Temperature of cold junction o° C.

s des G with a cement made of water glass and calcium carbonate. The molybdenite was then copper-plated over a small area at each

<sup>1</sup>Otto Reichenheim suggests the use of such a cement in Inaugural Dissertation, Freiburg, 1906.

of the exposed ends MM, and to these copper-plated areas were soldered copper wires, .2 mm. in diameter, so as to form thermal junctions with the molybdenite. The thermal junctions and the ends of the glass mounting were inserted into two brass vessels for containing the temperature baths of oil. The joints between the brass vessel and the glass mounting were made tight with the cement of water glass and calcium carbonate. The oil-baths were provided with stirrers driven by a motor. One of the baths was kept at 0° C., and the other bath was given various temperatures between 0° and 200° C. The resulting thermoelectromotive force was measured by means of a potentiometer to which the copper wires LL led. The results are recorded in Table VIII., and plotted in the curve of Fig. 9.

Table VIII.

Thermoelectromotive Force of the Copper-Molybdenite Couple, "E" the Cold Junction being kept at Zero.

Temperature of Hot Junction.	E.M.F. in Millivolts.	Temperature of Hot Junction.	E.M.F. in Millivolts.	Temperature of Hot Junction.	E.M.F. in Millivolts.
10.1	- 7.5	59.2	-42.5	133.2	- 90.7
14.3	-10.7	67.4	-48.6	141.9	- 96.9
16.2	-11.5	70.8	-51.2	156.8	-106.8
18.7	-13.8	76.0	-54.1	166.9	-113.2
21.5	-16.0	80.8	-57.2	176.8	-119.0
24.1	-17.6	99.2	-68.4	179.0	-120.0
25.6	-18.5	109.3	-75.2	180.9	-121.5
33.1	-24.6	111.6	-77.2	188.5	-126.2
36.2	-25.9	116.3	-79.2	192.7	-128.7
41.9	-31.5	118.7	-83.2	195.0	-130.0
51.1	-36.7		100		100

The negative sign before the E.M.F. in Table VIII. indicates that this specimen of molybdenite is thermoelectrically *negative* with respect to copper; that is to say, the current at the hot junction flows from the molybdenite to copper.

A slightly different form of mounting was employed for specimens A, B, C and D. These specimens, which were cut from two different large crystals of molybdenite, were each I cm. wide, 5 cm. long and from .5 to I mm. thick, and were mounted in corks. Each cork 4.5 cm. long, was split lengthwise, and one of

the longitudinal half-corks was grooved out to contain the molybdenite. The two half-corks with the molybdenite between were put together again and cemented with plaster of Paris, so as to leave 2 or 3 mm. of molybdenite protruding from each end of the cork. These small areas were then copper-plated, and copper wires .2 mm. thick were soldered to the copper-plated areas, so as to form thermal junctions. The four corks containing the specimens A, B, C and D were inserted in round holes in two copper vessels for containing the temperature baths of oil, so that the junction at one end of each specimen should be in the hot bath, while the junction at the other end was in the cold bath. The cold bath was kept at 20°C.; the hot bath was given various temperatures between 20° and 100° C. The thermoelectromotive force of each couple was measured on a potentiometer. The results for A, B, C and D are contained in Table IX., and are plotted in Fig. 10. For comparison a part of the curve obtained for E is also plotted in Fig. 10.

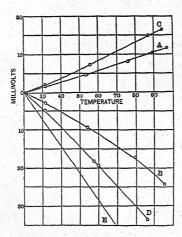


Fig. 10. Thermoelectromotive force of five copper-molybdenite couples, for various temperatures of hot junction. Temperature of cold junction 20° C.

Some of the specimens (B, D and E) are thermoelectrically negative with respect to copper, while the other specimens (A and C) are thermoelectrically positive with respect to copper. The thermoelectromotive force per degree differs largely with the different specimens, as may be seen by a reference to Table X., which con-

TABLE IX.

Molybdenite-Copper Junctions A, B, C, D. The Cold Junction was at 20° C. The Hot Junction was at Temperature T° C. The Thermoelectromotive Force V is in Millivolts.

Juncti	ion A.	Junct	ion B.	Junct	ion C.	Junction D.		
T	ν	T	$\nu$	T	V	T	$\nu$	
31.9	1.45	31.6	- 2.70	31.7	2.01	31.6	- 4.81	
53.5	4.63	54.1	- 9.21	55.2	7.20	57.5	-17.9	
76.6	8.21	80.0	-17.1		2.7	59.8	-19.4	
89.4	10.4	87.4	-20.0	87.2	14.9	86.7	-33.7	
97.1	11.5	95.3	-24.2	94.4	16.6	2.0		

tains the thermoelectromotive force per degree of the different specimens of molybdenite against copper, and against lead (obtained from the known value of the lead-copper junction). For comparison, Table X. also gives the thermoelectromotive power of some other remarkable thermoelectric elements.

TABLE X.

Substance.	Thermoelectromotive per Degree Cen	Authority.		
	Against Copper.	Against Lead.		
Molybdenite A.	110	113	Present experiment.	
B.	-230	-227	- ((	
C.	175	178	" "	
D.	-415	-413		
E.	-720	-717	" "	
Silicon.		-400	Frances G. Wick. 1	
Bismuth.	1 80	- 89	Matthiessen.2	
Antimony.	The state of the state of	26		
Tellurium.		502	**	
Selenium.		807	"	

The comparison shows that these specimens of molybdenite have very large thermoelectromotive force against copper or against lead. The specimens D and E were found to be at the extreme negative end of the thermoelectric series.

The great variability among the specimens studied may be due to an admixture of small quantities of some other substance with

<sup>&</sup>lt;sup>1</sup> PHYS. REV., Vol. 25, p. 390.

<sup>&</sup>lt;sup>2</sup> Everett, Units and Physical Constants.

the molybdenite, or it may be due to structural differences from point to point of the crystal. I have not yet investigated the question of the cause of the variability of the phenomenon. The differences in the specimens could not have arisen from the copper-plating or from the heat employed in soldering the junctions, because the specimens A, B, C and D were tested before the copper-plating and soldering were done, and by means of the preliminary test were classified as positive, negative, positive and negative respectively; which agrees with the determination after soldering.

The preliminary test was made by touching the specimens with two copper wires connected to a galvanometer, one of the wires being slightly warmer than the other. This preliminary test proved very interesting in that it shows that one may find all over many of the pieces cut from a crystal of molybdenite points where the substance is thermoelectrically positive and other points where it is thermoelectrically negative. These positive and negative points sometimes lie so near together that with a fine-pointed exploring electrode connected to a galvanometer and warmed by heat conducted from the hand one may find the deflections of the galvanometer reversed from large positive values to large negative values on making the slightest possible motion of the pointer over the crystal.

Explorations of this kind failed to show any definite orientation of the thermoelectric quality with respect to the crystallographic axes.

The existence of small thermoelectrically positive and negative patches in a piece of the molybdenite may indicate that the thermoelectromotive force measured by attaching wires to the specimen is too low on account of the inclusion under the electrodes of both positive and negative areas which would partially neutralize the thermoelectric action against another electrode. It may be, therefore, that the contact electrode as it is employed in the use of the molybdenite as a rectifier would be subjected to much larger thermoelectromotive forces than those revealed in the soldered connection experiments.

It may be said in passing that the specimens D and E, with the soldered connections, still showed the phenomenon of rectification when used with alternating currents, even when the two junctions

of the copper with the molybdenite were in oil-baths at the same temperature as the room and the oil in the baths was vigorously stirred with motor-driven stirrers. The rectification in this case was, however, very imperfect.

Temperature Coefficient of Resistance. — Another interesting thermal property of the molybdenite is its temperature coefficient of resistance. A preliminary report on this coefficient is here given. Two specimens of the molybdenite were made into the form of resistance thermometers, by depositing heavy copper-plated areas near the two ends of thin pieces of the molybdenite and soldering thin copper strips to the copper plate. For insulation a thin strip of mica was placed over the molybdenite, and one of the copper leads was bent back over the mica so that both leads ran away parallel with the mica insulation between. The whole conductor was then placed between two mica strips and inserted in a flattened brass The tube was then mashed tight together so as to securely clamp the molybdenite and its leads. The end of the tube adjacent to the molybdenite was soldered up. The leads were brought out at the other end of the tube and connected to binding posts insulated by a hard rubber head from the tube.

The two molybdenite resistances thus mounted are called No. 50 and No. 51. The dimensions of the molybdenite used in No. 50 were not recorded. The molybdenite in No. 51 was .65 cm. wide by .7 cm. long; the thickness was about .3 mm.

The resistances of these two conductors were measured at various temperatures with the aid of a Wheatstone bridge. They showed no evidence of rectification. In making the measurements it was necessary to keep the current small so as to avoid electrical heating of the conductors. With successive heatings and coolings the resistance of the molybdenite showed small progressive changes, which, however, after some months, almost disappeared. When the resistance of the two specimens of molybdenite had settled down to a practically steady condition, the values plotted in Fig. 11 were obtained. The curves marked "50" and "51" give the resistance of No. 50 and No. 51 respectively. The ordinates for these curves are at the left margin of the diagram, and are in ohms. The curves "C 50" and "C 51" are for the reciprocals of the resistance

of No. 50 and No. 51 respectively. The ordinates for these curves are at the right hand margin of the diagram.

Each of the specimens has a large negative temperature coefficient of resistance. With No. 50, for example, the resistance at  $93.1^{\circ}$  C., is 229 ohms; at  $0^{\circ}$  C., the resistance is 561 ohms; at  $-76^{\circ}$ , the resistance is 3.051 ohms; and at the temperature of liquid air, the

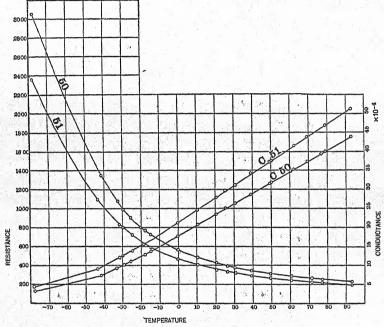


Fig. 11. Effect of temperature on electrical resistance of molybdenite.

resistance of this specimen was found to be over 6,000,000 ohms. This last value is not plotted on the curves.

It is interesting to note that between — 15° and 93° the temperature-conductance curve of each of the specimens is a straight line.

At 0° C. the resistance of each of the specimens decreases about 1.53 per cent. per degree centigrade increase of temperature. At 20° the decrease of resistance per degree increase of temperature is 1.19 per cent.

A previous determination of the resistance of molybdenite has been made by Otto Reichenheim. He did not solder on his con-

<sup>1</sup>Otto Reichenheim, Inaugural Dissertation, Freiburg, 1906.

nections but led the current into the specimen through contact electrodes and found that the resistance depended on the contact pressure. His data are, therefore, not comparable with mine, but I find that one of his specimens, measured parallel to the direction of cleavage, gives the conductance a linear function of the temperature between 19.5° and 92.5° C. with a slope not very different from that obtained in the present experiments.

The large thermoeletromotive force of the molybdenite against the common metals, together with its large negative temperature coefficient of resistance, lends plausibility to the hypothesis that the rectification is due to thermoelectricity. For if we pass an electric current through the rectifier and the current begins to make its way through a small area at the contact, this small area is heated and decreases in resistance so that the greater part of the current flows through this particular small area, heating it still more, while the portions of the contact through which the current has not started remain cool and continue to offer a high resistance. The effect of this action is to confine the heating to an extremely small area, which is the condition necessary for the extremely rapid and efficient action of the rectifier. That there is, however, strong evidence against this explanation of the phenomenon is, I think, made clear in the succeeding experiments.

EXPERIMENTAL FACTS ADVERSE TO THE THERMOELECTRIC EXPLANATION OF THE PHENOMENON OF RECTIFICATION.

The Thermoelectric Effect Opposite to the Rectification. — A number of experiments with different specimens of molybdenite were made, in which the rectification and the thermoelectric effect could be simultaneously studied. A diagram of the arrangement of apparatus is given in Fig. 12. The specimen of molybdenite is shown at M and was held down upon a wooden base by a spring clip. One end of each specimen, which were easily interchangeable in the apparatus, was electroplated with copper at S. To this copperplated area a copper lead was soldered. A copper rod C, supported as in Fig. 3, was brought into contact with the part of the molybdenite distant from the soldered junction. The molybdenite and the contact

<sup>&</sup>lt;sup>1</sup> Described as Stab II., p. 27 of the Dissertation.

were put in an electric circuit containing a microammeter or galvanometer at A and a source of variable alternating potential at V. The alternating potential V could be applied or omitted by closing or opening the switch at T. A small heating coil was wound on the rod C, and another similar heating coil E was wound on a second copper rod, placed immediately below the contact of C with M.

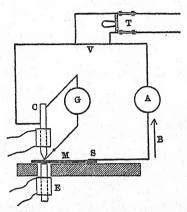


Fig. 12. Apparatus for comparison of rectified current with thermal current.

An auxiliary thermal junction, formed by a small constantan wire attached to the lower end of the copper rod C was connected to a second galvanometer shown at G, for use in a later experiment.

The copper rods C or D could be heated by the surrounding coils, and the thermal current in the circuit through the molybdenite or the circuit through the constantan could be read on the galvanometers A or G. Also the rectified current obtained by applying the alternating voltage V could be read on the galvanometer A. When the thermal current or the rectified current through A is in the direction of the arrow B the molybdenite, following the usage in thermoelectricity, is said to be *positive*. When the current in A is in the direction opposite to the arrow B, the molybdenite is said to be *negative*.

The results obtained with a number of specimens of molybdenite when heat was applied *above*, and when heat was applied *below* and when the *alternating voltage* was applied are contained in Table XI.

TABLE XI.

Sign of Molybdenite, when Heated Above or Below and when Subjected to Alternating Voltage.

Specimen No.	Heated Above.	Heated Below.	Under Alt. Voltage.
75	+		
81	+		
Turned over.	+	· · · · · · · · · · · · · · · · · · ·	
93	× =	+	+
Another point.	<u> </u>	<u> </u>	+
Turned over.		. 10 14 <u></u> . 11.	1 +
78	+	+	+
Another point.	+	<u>i</u> .*	
"	+	+	_
94	<u></u>	_	+
Another point.		+	
"	_	1	+

From this table it appears that the thermoelectric voltage when the junction is heated by heat conducted from above, in twelve out of the thirteen cases tried, is opposite to the direct voltage obtained when an alternating current is passed through the junction. When the heat is conducted to the junction from below, through the molybdenite, the thermoelectromotive force in four cases is opposite to the rectified voltage and in nine cases is in the same direction as the rectified voltage. In only one case, one point of no. 78, is the rectified voltage in the same direction as the thermal voltage both when the junction is heated from above and when it is heated from below.

In all of these cases the heat was applied in the neighborhood of the same junction and there was no opportunity for heat to get to the other junction by conduction, on account of the great distance of the other junction from the source of heat. To make this the more certain this distant junction was in some cases submerged in an oil-bath.

So far as I have been able to learn, this phenomenon of the reversal of the thermoelectromotive force at a junction, conditioned on whether the heat is conducted to the junction through one element of the junction or the other element of the junction is novel. It may be explained by the assumption of another thermal junction of oppo-

site sign in the molybdenite itself below and in the immediate neighborhood of the copper-molybdenite junction. This assumption is plausible because it has been shown above that the molybdenite with which these experiments were performed is thermoelectrically an extremely heterogeneous substance. On the other hand, the phenomenon may also be explained on the theory that the direction of the thermoelectromotive force is determined by the direction of the flow of heat.

Whatever the explanation of the dependence of the sign of the thermoelectromotive force on the manner of applying heat, it is seen that the thermoelectromotive force is usually opposite in sign <sup>1</sup> to the electromotive force produced by sending an alternating current through the junction.

By applying the heat from above and at the same time applying the alternating voltage one can make the thermal current and the rectified current neutralize each other. The opposition of the sign of the rectified current and the thermal current renders the thermoelectric explanation of the phenomenon of rectification highly improbable.

Effort to Detect Heating of the Contact of the Rectifier. — With the aid of the auxiliary thermal junction of copper-constantan placed at the contact of the copper with the molybdenite, as shown in Fig. 12, an effort was made to detect heating of the copper-molybdenite junction by the alternating current which was being rectified. When the rectified current was 118 microamperes, the heating shown by the copper-constantan junction did not exceed .o1° C. When on the other hand, as a control experiment, heat was applied to the copper-molybdenite junction from below so as to be conducted through the molybdenite and through the copper-molybdenite junction to the copper-constantan junction, the heating shown by the auxiliary copper-constantan junction was 11.4° C., while the thermal current from the copper-molybdenite junction was only .2 micro-

<sup>1</sup> In a series of experiments with silicon-steel, carbon-steel and tellurium-aluminum, L. W. Austin has found that the rectified current generally flows in opposite direction to that produced by heating the junction. In his experiments (Bulletin of the Bureau of Standards, Vol. 5, No. 1, August, 1908) the heat was applied by a soldering iron brought into contact with the low resistance metal, and therefore corresponds to heat conducted from above in these experiments.

ampere. In both the case of the rectified current and the case of the application of heat from below the heat had to be conducted from the point of rectification to the auxiliary junction. Therefore, with a rise of temperature of the auxiliary junction 1,100 times as great as the rise shown during the rectification, the thermal current in the copper-molybdenite circuit was 1/500 of the rectified current; that is to say the rectified current, for a rise of temperature of 1/100 of a degree of the auxiliary junction (being approximately a linear function of the temperature) was less than 1/500,000 of the rectified current from an alternating current producing the same rise of temperature.

From this experiment, also, it seems to the writer that the hypothesis that the action of the rectifier takes place through the intermediation of thermoelectricity is improbable.

The expenses of this research were in part defrayed by a liberal grant from the Bache fund of the National Academy, for which the author wishes to express his sincere thanks.

Experiments are still in progress.

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December 21, 1908.

## ATMOSPHERIC RADIOACTIVITY IN CALIFORNIA AND COLORADO AND THE RANGE OF THE $\alpha$ -PAR-TICLES FROM RADIUM B.<sup>1</sup>

By FREDERIC A. HARVEY.

THIS paper is an account of an investigation of atmospheric radioactivity at Berkeley California, and Denver, Colorado. The work is of interest in itself, since no previous investigation of this character has been made in these localities; and several new results have also been obtained, including the proof that radium B gives off α-rays of very short range, and the measurement of this range.

The earliest investigations on the subject of atmospheric radioactivity were made by Elster and Geitel.3 They found that a charged body loses electricity faster in the open air than can be explained by leakage across its supports and that this was due to a slight ionization of the air, which always exists. In the light of the recent discoveries with regard to radioactivity it was seen that this ionization might be caused by some radioactive substance in the atmosphere. To test this they exposed a negatively charged wire gauze in the open air. After an exposure of a few hours the wire gauze was placed in the ionization chamber of an electroscope and it was found that an active deposit had collected on the gauze. The amount of active deposit collected was greatly increased by using a long wire and changing the negative potential from four hundred to several thousand volts. The material of the wire had no effect on the amount of active material collected. The activity decayed in a few hours in a manner resembling that of thorium X. The decay was not hastened by heating. The active deposit could

<sup>&</sup>lt;sup>1</sup>Submitted in partial satisfaction of the requirements for the degree of Ph.D. in the University of California.

<sup>&</sup>lt;sup>2</sup>A brief note containing some of the more important points has already been published by the author. Phys. Zeitschr., 1909.

<sup>&</sup>lt;sup>3</sup>Elster and Geitel, Phys. Zeitschr., 3, p. 76, 1901, and p. 574, 1902; also 4, p. 522, 1903.

be transferred to a piece of leather and when concentrated in this form was sufficiently active to make a barium-platino-cyanide screen glow quite perceptibly to the rested eye, or give a shadow picture through a sheet of aluminium o. 1 mm. in thickness. All of these properties tended to show that the material was of the same nature as the active deposit collected from radium or thorium emanation. The amount of active material collected in caves and holes, where the air had been long stagnant, was much greater than in the open air. Meteorological conditions, such as fog, strong winds, temperature, and barometric height, were found to exert a marked effect on the amount of active material collected.

The work of Rutherford and Soddy¹ on the time rate of decay of thorium X has been extended until it is now generally accepted that each radioactive substance loses its activity according to some exponential law. Thus it is estimated that radium would lose half of its activity in about 1,760 years, whereas, radium A sinks to half-value in only three minutes. Where an active deposit consists of several radioactive components the total activity is made up of the sum of the activities due to these components. The usual method of analysis is to compare the curve showing the rate of decay of the active material with the curves of decay of the transformation products of radium, thorium and actinium, which are known with considerable accuracy. The method is more or less "cut and try" until a combination is found which will make the calculated and experimental results agree.

It is of importance to find the source of the emanation present in the air. Working toward this end Bumstead and Wheeler <sup>2</sup> found that the gas drawn from the surface soil at New Haven contained a radioactive gas apparently identical with radium emanation. Thorium emanation was not discovered because its life is shorter than the necessary time which elapsed in transferring the gas to the testing apparatus. Later Dadourian <sup>3</sup> exposed a negatively charged wire in a hole dug in the ground, at New Haven, into which fresh air was continually drawn from the surrounding soil. He found

<sup>&</sup>lt;sup>1</sup> Rutherford and Soddy, Phil. Mag., September and November, 1902.

<sup>&</sup>lt;sup>2</sup> Bumstead and Wheeler, Amer. Jour. Sc., Vol. 17, p. 97, February, 1904.

<sup>&</sup>lt;sup>8</sup> H. M. Dadourian, Amer. Jour. Sc., Vol. 19, p. 16, January, 1905.

undoubted evidence of thorium emanation in the soil gases. Eve has shown that the amount of radium salts distributed through the earth's crust is of the right order of magnitude to account for the emanation in the atmosphere.

The nature of the emanation which produces the phenomena of atmospheric radioactivity has been the subject of investigation by many observers with apparently diverse results. The usual method is to observe the rate of decay of the active deposit collected on a negatively charged wire exposed in the open air and compare it with the known and different rates of decay of radium, thorium and actinium transformation products. Allen working at Montreal and Cincinnati came first to the conclusion that the emanation is identical with that from radium, but later became convinced, owing to the diverse values of the half-period of decay (viz., the time taken for the decaying radioactive substance to lose half of its initial activity) of the active deposit, that it is a mixture, in varying proportions, of the emanations from radium, thorium and, possibly, actinium. Bumstead 2 showed that the active deposit collected on a wire exposed in the open air at New Haven is complex and that the thorium active deposit sometimes amounts to 15 per cent. of the total. Blanc 3 found that at Rome a very large percentage of the active deposit, from 50 to 70 per cent., collected on a wire exposed at a potential of - 500 volts, was due to thorium transformation products. The exposure in this case was long; nearly three days.

The objects of the present investigation are as follows: (1) To carry out for Berkeley, California, investigations similar to those which have been made in other localities as to the effect of meteorological conditions and as to the nature of the active deposit collected on a negatively charged wire exposed in the open air. (2) To determine the conditions governing the proportion of the components of the active deposit since this proportion was found to be variable. (3) To compare the active deposit obtained at Denver, Colorado, with that obtained at Berkeley. (4) To measure the range of the a-particles given off by the active deposit, particularly the range of

<sup>&</sup>lt;sup>1</sup> S. J. Allen, Phil. Mag., December, 1904. Phys. Rev., June, 1908.

<sup>&</sup>lt;sup>2</sup> H. A. Bumstead, Amer. Jour. Sc., Vol. 18, July, 1904.

<sup>&</sup>lt;sup>3</sup> G. A. Blanc, Phil. Mag., 13, p. 378, March, 1907.

the very easily absorbed radiation and to determine to what component this radiation is due.

The usual method for collecting the radioactive material was used, viz., a wire charged to a negative potential of a few thousand volts, was exposed in the open air for several hours. The wire was of copper, No. 22, B. and S. gauge, about 14 meters in length, supported about four meters from the ground, in the earlier experiments. Later the length was increased to 38 meters, the distance from the ground to about 5 meters, and the wire stretched in a position where winds from all directions could reach it easily. For insulating supports thin ebonite rods, about 40 cm. in length, were used. It was found that in damp weather a thin coating of vaseline put on the hot rods would greatly improve the insulation, as a film of moisture does not collect as readily on the vaseline as on the ebonite. The potential of the wire was maintained at first by means of a water-dropper and later by means of a motor-driven Wimshurst machine, Tudsbury patent. The Wimshurst machine worked more satisfactorily in damp weather than the water-dropper. The potential was measured by means of a Braun electrometer reading directly in volts.

In order to analyze the active deposit it is first necessary to obtain observations which show its rate of decay. This decay, always measured by means of the ionization produced by the  $\alpha$ -rays, was followed by several methods:

1. By means of an aluminium-leaf electroscope with sulphur insulation. The rate of fall of the leaf was measured in three ways. (a) The image of a circular scale, graduated in degrees, of radius equal to the length of the aluminium leaf, was superimposed on the leaf by means of a half-silvered mirror, placed at an angle of  $45^{\circ}$  in front of the observing telescope, and readings of the position of the leaf were taken at regular intervals. A curve was then plotted with positions of the leaf and times of observation as coördinates. The tangents to this curve give the rate of fall of the leaf. Any error in reading is self-correcting by this method and tangents can be determined within about one per cent. (b) A small Gurley comparator, reading to  $\frac{1}{100}$  mm, was used. Readings were taken of the distance moved by the end of the leaf, at about  $45^{\circ}$  deflection,

during regular intervals of time. (c) This method differs from the first only in that a circular scale, with vernier, was fixed to the tube of a telescope and the angular motion of the leaf read by turning the cross wires until one of them coincided with the aluminium leaf. When a very large amount of active material had been collected sufficient accuracy could be attained, without plotting the curve of position, by merely observing the angular fall of the leaf during short, equal intervals of time, from one to ten minutes. The electroscope was calibrated by noting the rate of fall over various parts of the scale when a constant source of ionization, viz., the  $\alpha$ -rays from uranium oxide, was used. The deflection of the leaf was kept between the limits 45° and 20°, as over this part of the scale the rate of fall is most uniform. The potential of the charged system for a deflection of 20° was about 500 volts, which was more than sufficient to secure the saturation current for the degree of ionization obtained.

- 2. By means of a quadrant electrometer made by Max Kohl after the design of Elster and Geitel, which was connected up in the usual way; one pair of quadrants earthed, the other pair connected to a plate or rod in the ionization chamber and the needle charged to a potential of 100 volts. The leak to the quadrants was then measured by noting, with a stop watch, the time taken for the spot of light to travel over a definite number of divisions on the scale—always the same divisions.
- 3. The null method described by S. J. Allen¹ was used. In this method the unknown ionization is balanced against a known ionization produced by a thin layer of uranium oxide. The parallel plates or concentric cylinders between which is the unknown ionization, are connected to one end of a battery of small cells while the uranium oxide plates are connected to the other end, the middle point being earthed in such a way that the current to one pair of quadrants from the unknown is of opposite sign to that from the standard. The surface of the uranium oxide exposed is varied until these two currents are just equal, when there is no change in the deflection of the needle. The instrument is calibrated for different amounts of surface exposed.

<sup>&</sup>lt;sup>1</sup>S. J. Allen, Phil. Mag., December, 1907.

The first method was the least subject to external disturbing influences and was sufficiently accurate except when a comparison of the amount of activity of two substances was desired. In consequence it was most used. The other methods, however, were useful as checks. It is not possible to distinguish the curves obtained by one method from those obtained by another.

Percentages of thorium excited activity were determined in the following manner: Several sets of observations on the rate of decay of the active deposit from radium for a three-hour exposure of a negatively charged wire (potential - 5,000 volts or over) to radium emanation in the bell-jar were taken, using the ionization produced These sets of observations were reduced to a common scale and averaged. From these average values a standard curve was plotted for the rate of decay of an equilibrium mixture of radium A, B and C. The agreement among the several sets of observations was good, the divergence being not more than two or three per cent. in any case. The standard curve was then made to agree with the curve under examination at the thirty-minute point and the activity due to the radium deposit calculated for the threehour point. Using this value as a first approximation the difference between it and the experimental value gives the activity due to the thorium active deposit at the three-hour point. From this the thorium activity at the thirty-minute point was calculated, using the equation  $I = I_0 e^{-\lambda t}$ . Thorium active deposit loses half its activity in about eleven hours, hence  $I = \frac{1}{2}I_0 = I_0e^{-11\lambda}$  and  $\lambda = .063$  when t, the time, is in hours. The part of the activity due to the radium deposit could now be determined for the thirty-minute point. Using this more accurate value the radium activity at the three-hour point was re-determined from the standard curve, and using the difference between this second approximation and the experimental value as the activity due to the thorium active deposit at the three-hour point the initial amount was determined. This divided by the total initial activity gave the percentage of thorium excited activity to a very close approximation. Correction for the normal leak of the electrometer or electroscope was of course made in each case. When observations had been carried on over a length of time as great as eleven hours the amount of thorium excited activity could be at once determined, since usually all of the radium excited activity disappears within six hours from the time of ending the exposure. Calculations by the first method showed very good agreement with those by the second.

## OBSERVATIONS MADE IN BERKELEY.

The half-value period of the active deposit obtained on a negatively charged wire exposed in the open air was not constant, but varied between wide limits. In particular (see Table I.) the half-period varied from 33 minutes to  $5\frac{1}{2}$  hours. As will be shown later the active deposits can be accounted for on the supposition that they consist entirely of radium and thorium transformation products and this change in the period is due to the varying proportions of the components. It takes a little over three days for the thorium active deposit, which will collect on a negatively charged body to reach its maximum value, provided all the conditions are constant during this interval, which is impossible in an open air exposure, and the period will increase with the percentage of thorium deposit. Thus the period depends to a certain extent upon the time of exposure.

This variation of the half-period has also been observed by S. J. Allen.<sup>1</sup> A large part of the present investigation had been completed before Allen's work appeared. The agreement at the two localities is good except that the period varies between wider limits at Berkeley, an effect due to two causes. The present method allows that observations be commenced sooner after the discharge of the wire than does that of Allen. This makes it possible, at times, to observe the activity due to the very rapidly decaying radium A and consequently shortens the period observed. Greater percentages of thorium active deposit must account for the extension of the other limit.

The agreement between the calculated values, assuming that the excited activity is due to radium and thorium and the observed values, is very good. After the percentage of thorium active deposit initially on the wire had been calculated, according to the method described above, the curve  $I = I_0 e^{-\lambda t}$  was plotted, where

<sup>&</sup>lt;sup>1</sup>S. J. Allen, Phys. Rev., Vol. 26, p. 483, June, 1908.

TABLE I.

No. of Curve.	Half- Period.	Per cent. of Th Initially.	Time of Exposure	Poten- tial.	Remarks.
1	44 min.	1.8	3½ hrs.	3,300	Clear, light east wind, dry.
					Barom, steady, nearly logarithmic.
2	47 "	3.0	4 "	3,300	ditto.
3	43 "	4.0	3 "	3,600	North wind, clear, hot, very dry,
		- 1		-	nearly logarithmic.
4	34 "	6.0	3 "	5,000	North wind.
5	72 ''	12.8	123 "	4,000	North wind, over-night exposure,
				*	with strong wind.
6	58 ''	12.8	141 "	4,000	ditto.
7	48 ''	22.0	3 "	3,800	Light west wind.
8	66 ''	19.0	4 "	3,250	Light southwest wind, very clear,
					absolutely logarithmic.
9	89 ''	46.0	51 "	3,500	Light west wind, clear.
10	54 ''	32.0	3 "	4,500	Strong west wind, clear.
11	49 "	21.0	3 "	4,500	Light north wind, good logarith-
					mic curve.
12	60 ''	11.0	3 "	4,800	ditto.
13	66 ''	29.4	12 "	4,000	North wind, strong.
14	59 ''	13.0	3 "	4,500	Still, clear.
15	61 ''	34.0	13 ''	> 5,000	Clear, west wind, light.
16	36''	26.0	41 "	4,500	Cold and foggy, west wind
				1 7 7 7 7	strong.
17	4 hrs.	56.0	13 "	1,500	Cold and foggy, barom. low and
1					falling.
18	44 min.	3.8	3 "	5,000	Same, except barom, rising rap-
				1 2	idly.
19	45 "	2.7	3 . "	5,000	ditto.
20	51 "	11.6	3 "	1,700	Cold, damp, still.
21	43 ''	7.2	3 "	4,000	ditto.
22	90 ''	?	12 "		Exposure with A.C. 2,200 volts
23	56 ''	9.2	18 "	> 5,000	North wind, very dry.
24	36 "	7.5	12 "	> 5,000	ditto.
25	$5\frac{2}{3}$ hrs.	70.3	22 "	500	ditto.
26	50 min.	11.7	43 "	4,000	Just after north wind.

 $\lambda = .063$  and t is expressed in hours. This gives the decay of the part of the activity due to the thorium deposit. From the standard curve for the decay of radium A, B and C, in an equilibrium mixture the decay of the part of the curve due to radium active deposit was then determined, making the calculated and experimental values agree at the thirty-minute point. The thorium and radium excited activity decay curves were then added together and in prac-

TABLE II.

	0	7	I	1 1/2	2	3	- 6	11	18	24
I	182	110	64	35	15	2				
TT	6	5.5	5.5	5	5	5				
1 111	188	115.5	69.5	40	20	7				
IV	188	116	61	33	16	6	-			
1	185	113	70	37	21	2.5			7	
TT	5.5	5	5	4.7	4.5	4				
2 111	190.5	118	75	41.7	25.5	6.5				
IV	190.5	118	70	41	24	7	. 1			
Ι	260	160	90	46	30	-				
TT	10	9.5	9	8.5	8					
3 III	270	169.5	99	54.5	38					· .
IV	270	170	100	56	37			1		-
I	160	88	40	22	6				. 17	100
, II	10	9.8	9.6	9.3	. 9	(				
4 III	170	97.8	49.6	31.3	15					* 1
IV	170	94	47	27	14		1.0		- 1	
I	164	117	69	31	15	6	3	0	0	0
	24	23	22	21.5		19	17	12.3	6.7	5.0
5 11	1	1	1		21		=	12.3	6.7	1
III	188	140	91	52.5	36	25	20	12.3	6.7	5.0
IV	188	130	83	58.0	40	28	?		0.7	4.0
I	150	90	53	30	12	7	15	0		0
6 II	22	21	21	20	20	19	12		6	4.8
III	172	111	74	50	32	26	16	11	6	4.8
IV	172	110	71	54	40	28	16	11	6	4.8
I	138	67	41	23	12	6		1 8 1	A 100	
7 II	39	38	38	37	36	35				
111	177	105	79	60	48	41				
IV	177	105	77	58	48	41				
1	190	128	80	48	24					-
8 II	46	44	43	42	40		1.2			
111	236	172	123	90	64					ĺ
IV	236	168	124	90	64	1.5	1			1
I	85	56	36	20	10					
9 II	73	71	68	66	64			114		
III	158	127	104	86	74					
IV	158	127	108	91	73	100				- 1
I	127	61	39	27	11					
10 II	46	44	43	42	41					
111	173	105	82	69	52		1			
IV	173	106	82	61	51				;	
I	153	87	54	30	15			1		-
11 II	40	39	38	37	36			1 1 1 1		, 1
11 111	193	126	92	67	51			10.00		1
IV	193	127	89	66	50	100			4	,

TABLE II. — Continued.

		0	1/2	I	11/2	2	3	6	ıı	18	24
	I	53.4	37	23	13	7	2		-		Х.
12	II	6.6	6	6	6	5.5	5.5	-	1		
12	III	60	43	29	19	12.5	7.5				
	IV	60	44	30	19	13	8		1		
	I	110	66	40	21	11	4	?	0	0	. (
13	II	46	45	43	42	41	39	32	24	14	1.
13	III	156	111	83	63	52	43	_	24	14	1
	IV	156	109	82	64	54	45	32	23	14	9
	I	261	172	126	63	39	8				
	II	39	38	36	35	34	30				
14	III	300	210	162	98	73	38				
	IV -	300	210	148	100	73	36				
	I	173	93	55	32	17	4				
	II	97	94	91	88	86	80				
15	III	280	187	146	120	103	84				
	IV	280	187	141	117	103	85				
	I	210	82	50	30	14	5			0	
	II	74	72	69	67	65	61	-		21	
16	III	284	154	119	97	79	66	. *		21	
	IV	283	160	116	94	80	70			28	
	I	43	27	18	11	6	2	. ?	0	0	
	II	55	54	53	50	48	45	37	28	18	1
17	III	98	81	71	61	54	47	==	28	18	1
	IV	98	81	71	63	56	47	37	28	20	1
	I	190	111	65.5	32	17.5	8	<b>3.</b>	20	20	T
	II	7.5	7	6.5	6	5.5	5	* - 3			
18	III	197.5	118	72	38	23	13		-		
	IV	197.3	118	68	38	24	13				
	I	214	136	76.5	59	35	15				
	II	6	6	5.5	5	5	5				- 1
19	III	220	( X	1	64	1	20				
	IV	220	142 142	82	64	40	20				1.0
	I	152		82	30	40	6		4		
	II	20	88	54	1	16		- 1			1 9
20	III		20	18	18	16	16				100
	IV	172	108	72	48	32	22				
	I	172	112	82	54	36	25				1
	II	154	90	56	34	19	4				
21	III	12	12	11	11	11	10				
		166	102	67	45	30	14		1 10		
	IV	166	102	66	44	31	15				
	I	99	57	36	18	4 .	2		0		-
23	II	10	10	10	9	9	9	8	5		
	III	109	67	46	27	13	11	== .	5		
	IV	109	67	43	26	13	11	8	6	×12	

TABLE II. - Continued.

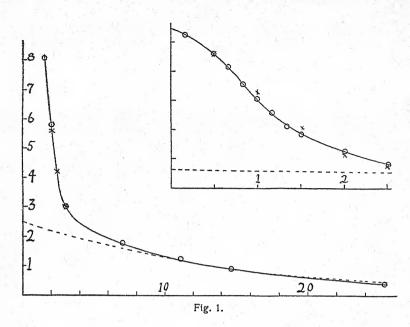
*	, 0,	1	I	11	2	3	6	II	18	24
I	185	83	55	31	14	3	?	0	-	- 1
O4 II	15	14	14	13	12	12	9	7.5		
24 111	200	97	69	44	26	15	=	7.5		
IV	200	97	62	40	26	14	9	7.5		
I	64	45	33	22	8	2	. 3	0		
25 II	151	145	135	132	130	124	103	75		
Z5 III	215	190	168	154	138	126		75		
IV	215	190	170	155	142	127	103	75		
I	468	280	174	101	47	14	0	0		
26 II	62	60	56	53	51	48	40	32		
Zo III	530	340	230	154	98	62	40	32		
IV	530	340	230	154	98	60	40	32		

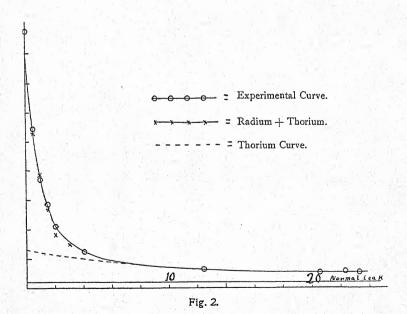
tically all cases the agreement with the observed values is closer than the limit of experimental error.

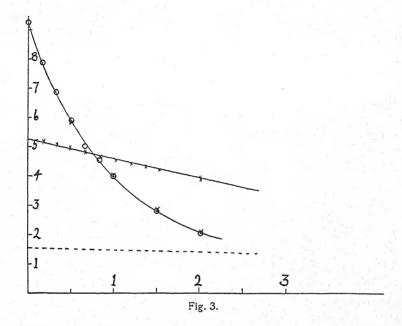
Table II. shows the agreement between the observed and calculated results. The number at the head of each column refers to the time, in hours, from the end of the exposure. The number at the left of each set of four rows refers to the number of the observation. The Roman numerals are as follows in each case: I. is the ionization due to the radium products; II. is that due to the thorium products; III. is the sum of I. and II. and gives the calculated activity; IV. is the observed activity. A few curves are given for illustration (see Figs. I-8, illustrating observations 5, 6, II, I2, I7, I8, I9 and 21 respectively).

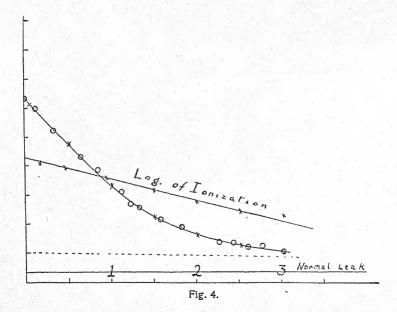
The percentage of thorium excited activity varies between very wide limits (see Table I.), the minimum obtained being 1.8, the maximum 70.3 per cent. of the total activity. The following general statements may be made regarding the conditions governing the percentage of thorium excited activity.

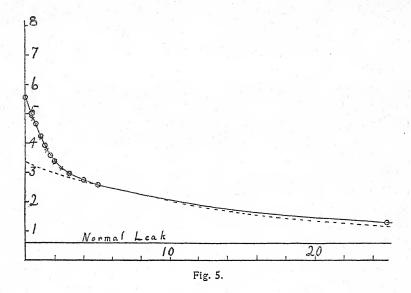
I. A much larger percentage of thorium excited activity collects on a wire exposed at a low potential than on one exposed at a high potential in the open air. This point has been thoroughly tested. Rows 20 and 21 of Table I. are a fairly good illustration of this although here the potential was not varied greatly. The results shown in row 20 were obtained when the potential was — 1,700

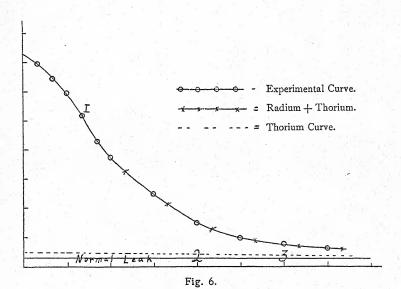


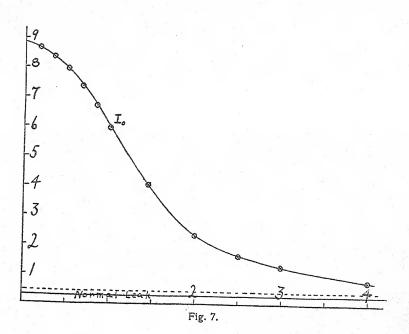


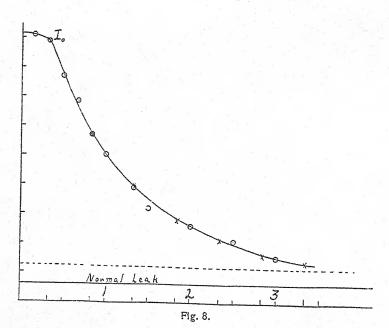












volts, in row 21 when it was — 4,000 volts. Atmospheric conditions were identical in the two cases and the two exposures occupied a total time of only seven and a half hours. Row 20 shows 11.6 per cent., row 21, 7.2 per cent. of thorium excited activity. Row 17 shows an unusually high percentage. The low potential, — 1,500 volts is partially responsible for this although here other conditions combine to cause the high percentage (see below). Row 25 which shows the highest observed percentage, 70.3 per cent., of thorium deposit is perhaps the most striking example. The observations shown in this row were taken under conditions very similar to those of row 23 and 24, i. e., during a north wind, when a low percentage would be expected (see below). The potential was very low, being only — 500 volts. The time of exposure was long but not greatly longer than that of the wire in observation No. 23.

This fact contains the explanation of the very large percentages, from 50 to 70 per cent., of thorium excited activity obtained at Rome by Blanc, who used a potential of only — 500 volts. It has long been known that this is not a sufficiently high potential to collect the maximum amount of active deposit on a wire exposed in the open air. These percentages, it is true, were obtained with very long exposures, and it takes a little over three days for the thorium active deposit to reach 99 per cent. of its final value. It is a very simple matter however to calculate the final per cent. of thorium deposit, which would have been collected on the wire had equilibrium been reached, from the time of exposure and the observed percent-Moreover this is a much more reliable method as it is very unlikely that the percentage of thorium excited activity would not change during a three-day exposure and this would produce irregularities in the curve which would militate against accuracy. Table III. the calculated percentage of thorium excited activity, had it reached an equilibrium is given under the heading per cent. Th. Corrected, and it is here conclusively shown that there is a very wide variation in the actual proportion of thorium excited activity to be collected from the atmosphere at different times, the minimum being 10.6 per cent., (row 24) and the maximum 76 per cent. (row 9). Sixteen out of the twenty-six values fall below the minimum set by

<sup>&</sup>lt;sup>1</sup>G. A. Blanc, Phil. Mag., 13, p. 378, March, 1907.

TABLE III.

No. of Curve. Hours of Exposure. Total Activity. Due to Ra. Th Corrected. Total Corrected.	Corrected. Barom.
Corr Corr Pee	3   7
1 3½ 188 182 6 190 30 220 13.	6 Steady.
2 4 190.5 185 5.5 191 25 216 11.	5 "
3 3 270 260 10 271 59 330 17.	8
4 3 170 160 10 167 59 226 26.	5 Rising.
5 12\frac{3}{4} 188 164 24 164 44 208 21.	
6 $14\frac{1}{2}$ 172 150 22 150 39 189 20.	6 Falling.
7 3 177 138 39 144 230 374 61.	5 "
8 4 236 190 46 196 209 405 51.	6
9 5 158 85 73 86 270 356 76	-
10 3 173 127 46 133 270 403 67	
11 3 193 153 40 202 235 437 54	Steady.
12 3 60 53.4 6.6 63 39 102 38.	2 "
13 12 156 110 46 156 87 243 35.	6 "
14 3 300 261 39 272 230 502 46.	0 "
15 13 280 173 97 173 173 346 50.	0 ""
16 $4\frac{1}{3}$ 284 210 74 216 308 524 59.	0
17 13 98 43 55 43 97 140 69.	3 Low and
	falling.
18 3 197 122 7.5 127 44 171 25.	7 Rising
	rapidly
19 3 220 214 6 223 35 258 13.	6 ditto.
20 3 172 152 20 158 118 276 42.	8 Falling
	slightly.
21 3 166 154 12 160 70 230 30.	2 Steady.
23 18 109 99 10 99 19 118 16.	1 Steady.
24 12 200 185 15 185 22 207 10.	6 Rising.
25 22 215 64 151 64 198 262 75.	8 "
26 4 <sup>2</sup> 265 234 31 238 120 358 33.	6 Steady.

Blanc, viz., 50 per cent. I think that without doubt the lower value of the percentage of radium emanation given by Blanc, for Rome, compared with that by Dadourian for New Haven is due to the fact that Blanc did not use sufficiently high potentials, rather than the difference in locality.

An explanation of the cause of the higher percentages of thorium excited activity with low potential is somewhat difficult owing to the imperfect state of our knowledge as to the actual mechanism of the collection of the active deposit on a negatively charged wire; i. e.,

<sup>&</sup>lt;sup>1</sup> H. M. Dadourian, Amer. Jour. Sc., 25, p. 335, April, 1908.

why, when the neutral emanation expels a positively charged  $\alpha$ -particle it leaves behind a positive instead of a negative charge on the radium A particle. There must be, it would seem, a different rate of diffusion because of which most of the thorium A particles are drawn to the wire for a low potential while it requires a high potential to exhaust the surrounding air of its radium transformation products.

- 2. The percentage of thorium excited activity is very sensitive to barometric change. Observations 17, 18 and 19, represented by Figs. 5, 6 and 7 furnish a good illustration of this. The potential is, it is true, lower for Fig. 5, but the extreme change from 69.3 to 13.6 per cent. (see Table III.) of thorium deposit is not all accounted for by this difference. Observations 17 were taken just at the end of a long continued barometric fall, 18 and 19 immediately afterward when the barometer was rising rapidly. The percentage decreases from observations 18 to 19, although one was taken immediately after the other and conditions were exactly similar. This plainly shows the decrease of thorium excited activity during a rapid rise in the barometer. It is to be expected if we suppose the emanation to diffuse upward through the soil. An increase of pressure would tend to prevent the escape of the emanation into the air and as its period is so short, 54 seconds, the supply of thorium A would be cut off at once and the only active products which it would be possible to collect would be the thorium A, B and C already present in the atmosphere. These would of course be decreasing all the time. radium emanation, half-period 3.7 days, on the other hand, would persist much longer and keep up the supply of radium A. thus clear why the percentage of thorium active deposit is decreased by a sudden rise in the barometric pressure.
- 3. Another fact of interest for comparison is the following: D. Pacini, finds for a wire exposed over the Gulf of Liguria, for nine hours, that practically all the activity is due to radium, with scarcely a trace due to thorium. At Berkeley the west wind sweeps directly in through the Golden Gate, over the Bay of San Francisco and over about 2.4 miles of land to the Physics building, yet the percentages of thorium excited activity are much larger for this wind than for

<sup>&</sup>lt;sup>1</sup> D. Pacini, N. Cimento, 15, p. 24, January, 1908.

any other. The average of the equilibrium values of the per cent. of thorium excited activity, from Table III., for exposures 7, 8, 9, 10, 15 and 16, which were made during periods of west wind, is 60.8 per cent. The average of all other percentages except those from north wind exposures 37.9 per cent. The average of all percentages except for west wind exposures is 31.7 per cent. These percentages prove that either the air over the Pacific Ocean off San Francisco, does contain thorium emanation or that the West Berkeley tidal-marshes have an unusually high percentage of thorium salts. Opportunity has not yet presented itself to test the two possibilities.

The initial activity on the wire varied between very wide limits, the maximum being as much as seventy times the minimum. The greatest amount of active material was collected during a hot, dry, north by east wind. This wind is known in Berkeley as the "north wind" and is the only strong land wind. It attains a velocity of 20 or 30 miles an hour at times. There is a large area covered by volcanic springs, where Shasta, Tehama and Plumas counties, California, come together, about 180 miles from Berkeley. The north wind crosses this area and follows the course of the Sacramento River. It seems very probable that the increased activity, at such times, is due to radium emanation carried down from this region. This supposition is borne out by the fact that the greatest activity does not appear on the first day of the wind, which usually blows three days, and also by the fact that the increase in the activity is very largely due to radium products whereas there is not a corresponding increase in the activity due to thorium products. The short life of the thorium emanation would account for this latter. does not give the actual initial values of the activity on the wires as it is more convenient to have comparable numbers for the purposes of plotting, etc., but it will be seen that the sets of observations 1 to 6, 23 and 24 show a low percentage of thorium excited activity. These observations were taken during periods of north wind. The results shown by curve 25 apparently present an exception to this as they also were taken at the time of a north wind but here the high percentage is due to the low potential as explained above. The low percentage shown in rows 18 and 19 is also explained above.

The north wind is accompanied by very disagreeable physiological effects and it has been suggested that these may be due to the abnormally large amounts of radium emanation in the air. Experiments on the effect of radium emanation on animal life would be comparatively easy to try and might yield some interesting results.

The north wind is also accompanied by a rise in temperature and low relative humidity. Ordinarily, at Berkeley, the relative humidity varies from 80 to 90 per cent., but at these times it may fall as low as 50 per cent.

The south wind is also a land wind, but is not accompanied by nearly such large amounts of active material. The relative humidity is so high that insulation is maintained with extreme difficulty and measurements hard to make.

The lowest activity accompanies the wind from the west, *i. e.*, from the ocean. Here also the relative humidity is high. The experiments of Elster and Geitel <sup>1</sup> showing that the greatest amount of active deposit was collected during a fog are not borne out at Berkeley. The fog here is not a land fog but is blown in from the ocean and is accompanied by a very low activity. The greatest amount of active material is collected when the relative humidity is low, *i. e.*, when there is a north wind as stated above. Attempts to discover a direct relation between humidity and amount of active deposit have not been successful as might be predicted since too many disturbing conditions enter.

The variation in temperature is so small at Berkeley that no effects due to it have been observed.

The statement is very generally made that "the height of the barometer was found to exert a very marked influence on the amount of excited activity to be derived from the air." This appears to need correction in its statement though not in its interpretation. It is not the actual atmospheric pressure which has an effect on the amount of active material but the history of the barometer for a few hours previous to and during the exposure. It has already been shown that a sudden rise in the barometer will cause a change in the relative amounts of thorium and radium deposits but not very

<sup>&</sup>lt;sup>1</sup> Elster and Geitel, Phys. Zeitschr., 4, p. 522, 1903.

<sup>&</sup>lt;sup>2</sup> Rutherford, Radioactivity, second edition, p. 518.

much change in the total amount of material collected. A long continued low barometer usually causes an increase in the amount of active material collected but the north wind, which, as has been said, brings the greatest amount, is almost always accompanied by a steady, high barometer.

It appeared from the earlier experiments that an uncharged wire did not collect a measurable amount of active deposit. true for a wire suspended near the Physics building and running parallel to its walls. In the later experiments a wire was stretched across the roadway, near the building, and it was found that considerable quantities of dust were collected. The uncharged wire was therefore tested again after an exposure of some 48 hours and a slight activity detected. This result again agrees with the work of Allen (loc. cit.) on the Radioactivity of a Smoke-Laden Atmosphere. It appears that the active particles collect on the dust or smoke particles which in turn collect on the wire. No such large amounts as Allen speaks of were at any time collected. A positively charged wire showed no signs of activity after a twelve-hour exposure. A wire connected to one terminal of a 2,200 volt alternating current circuit while the other terminal was earthed showed more activity than an uncharged wire and less than one charged negatively to the same potential.

In order to determine whether the fact that the wire is charged during an exposure has any effect on the period of transformation of the particles which collect on it the following experiments were tried. Two wires were exposed, side by side, charged to the same negative potential for five hours. At the end of this time they were brought in and the activity of one of them tested. The other was coiled in a convenient shape and hung in a bell-jar of small capacity, where it was maintained at the same negative potential it had when exposed. After two and a half hours its activity was tested and it was found to continue the curve of decay from the earlier wire without discontinuity. The experiment was repeated maintaining the wire when in the bell-jar positively charged, with the same result as for the negative charge. This shows that the charge on the wire does not have any effect on the period of transformation. The result might again have been predicted as, accord-

ing to the theory of radioactive transformations, no force of finite magnitude can alter the period of transformation.

Curves of the shape shown in Figs. 6 and 7, consisting at first of a convex upward part, are very similar to those called class 2 by S. J. Allen (*loc. cit.*). I have found that a curve of this type almost always results from an exposure made while the barometer is rising, and seldom from an exposure made under any other conditions. It is to be expected that a change in the barometric height would cause a change in the supply of emanation and hence a change in the equilibrium value of the mixture of products and hence an irregularity in the shape of the curve.

## OBSERVATIONS MADE IN DENVER.

During June and July, 1906, some measurements of the active deposit obtained from the atmosphere were made in Denver, Colorado, and as I am not aware of any published results from this locality they are given here.

The exposed wire was of copper, No. 18 B. and S. gauge about 12 meters in length and three meters from the ground. The potential was maintained by means of a water-dropper. After an exposure the wire was wound in the form of a helix and introduced into an aluminium-leaf electroscope, where the rate of decay was followed by the method 1a, described above.

The results do not differ essentially from those obtained at Berkeley except as to the effect of the direction of the wind. The greatest amount of active deposit was collected at the time of a high northwest wind but as this was the only strong wind during the two months over which the observations were extended, the direction cannot be regarded as having any very great importance. The amount of active material collected does not differ appreciably at the two places. Percentages of thorium excited activity and the half-period vary between about the same limits.

The observations were brought to an end by the maturing of the seed-pods on the cotton-wood trees. The blowing of the cotton made insulation a matter of extreme difficulty.

Of the exposures made, nine yielded useful results. The tables corresponding to Tables I. and III. follow.

TABLE D-I.

No. of Curve.	Hal Peri		Per cent. of Th Initially.		ne of osure.	Potential.	Remarks.
D-1	90 r	nin.		3	hrs.	4,000	High west wind.
D-2	30	66		3		4,500	ditto. Short period due to Ra. A.
D-3	60	"	50	15	6 6	4,500	Very high northwest wind.
D-4	53	66	27	4	66	4,500	Clear, still.
D-5	55	46	13.7	4	6.6	3,000	ditto.
D-6	48	"	8.0	31	66	4,250	ditto.
D-7	45	"	4.0	4	"	4,500	ditto.
D-8	50	"	2.5	3	"	3,700	Cloudy, still.
D-9	33	"	15.0	31		4,750	Light east wind, clear, short period
				1,18			due to Ra. A.

TABLE D-III.

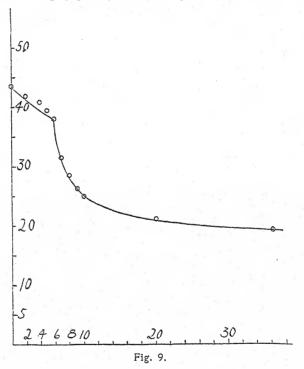
No. of Curve.	Hours of Exposure.	Total Activity.	Due to Ra.	Due to Th.	Ra Correc.	Th Correc.	Total Correc.	Percent. Th Corrected.
D-3	15 hrs.	540	270	270	270	440	710	62.0
D-4	4 "	130	95	35	98	159	257	62.0
D-5	4 "	127	109.6	17.4	113	79	192	41.0
D-6	31 "	180	165.6	14.4	173	72	245	29.4
D-7	4 "	400	384	16	396	73	469	15.6
D-8	3 "	440	429	11	452	65	517	12.5
D-9	31 "	380	323	57	334	317	651	48.7

## RANGE OF THE α-PARTICLES FROM THE ACTIVE DEPOSIT AND FROM RADIUM B.

It seemed desirable as a further proof that the active deposit collected on a negatively charged wire exposed in the open air consists of radium and thorium transformation products, to test the range of the α-particles. It was thought that the method proposed by Bragg <sup>1</sup> for a feebly active product might be used, for, as has been shown, wires can be obtained with a very low percentage of thorium excited activity and this amount might be calculated and the proper correction made. The method measures the range in terms of the stopping power of a screen of variable thickness covering the active substance. A wire was therefore exposed, the active deposit rubbed off with a piece of absorbent cotton moistened with ammonium hydroxide, a treatment which will further reduce the

<sup>&</sup>lt;sup>1</sup> W. H. Bragg, Phil. Mag., 11, p. 754, June, 1906.

percentage of thorium active deposit as this deposit is less soluble in ammonium hydroxide than that of radium. The cotton was then incinerated, the residue spread in as thin a layer as possible and its activity tested, first when the ionization chamber was directly exposed to its influence and then as very thin sheets of aluminium foil were placed over it. Readings were frequently taken with the naked deposit to obtain data from which the decay curve could be plotted. The time of all readings was recorded. The result obtained was very unexpected. Fig. 9 plainly shows the presence of a radiation which



is completely absorbed by from 6 to 10 layers of aluminium foil. It is evident at once from the curve that agreement among separate calculations of the full range cannot be expected by Bragg's method. The characteristic shown in the tables given by him, *i. e.*, an increase in the value of the product  $\rho d$ , *i. e.*, density times thickness, for full range, as the thickness of the foil was increased was shown to a very marked degree. Calculations for the range are all smaller than

would be expected and the calculation from the foil of greatest thickness gives a little less than one half the range of radium C.

The recent work of S. J. Allen  $^1$  explains this value. He has tested the range of the  $\alpha$ -rays from the active deposit obtained from the atmosphere and has shown that "where the rays are allowed to emerge in all directions to the normal the position (of maximum ionization) is much less than the range of the particle, being roughly one half." The above result is in agreement with this statement by Allen.

The product,  $\rho d$ , of the foil used to obtain the data for Fig. 9, was  $6.47 \times 10^{-5}$  for each sheet. Using the value of the stopping power of aluminium foil, in terms of air, given by Bragg, viz., foil for which  $\rho d = .00329$  is equivalent to 2.30 cm. of air, calculation shows that the easily absorbed radiation would be completely stopped by between 2.7 and 4.5 mm. of air. The values of the stopping power of aluminium foil obtained by S. J. Allen (*loc. cit.*) agree very well with that of Bragg, and show that it is about the same for rays from radium C, thorium and uranium. It is to be seen from Fig. 9 that nearly half of the ionization produced by the naked deposit is due to this easily absorbed radiation. The curve has been corrected for the natural decay of the deposit and the ionization chamber was made deep enough to allow the  $\alpha$ -particles from radium C and thorium C to run their full course.

It was of course desirable to determine which of the several components of the active deposit gives off this easily absorbed radiation. To do this, first, a wire was exposed for a long time in the open air in order to obtain a large amount of thorium active deposit. This deposit was allowed to stand for six hours before any tests were made, during which time all the radium products transformed into the inactive radium D. The data for an absorption curve were then obtained by adding layers of aluminium foil and taking readings of the ionization. The absorption curve, corrected for the natural decay, showed no trace of the easily absorbed radiation. The radiation, then, cannot be due to thorium A nor any of its successive transformation products. This result was expected as Fig. 9 shows such a large part of the total ionization to be cut off by the first ten sheets of foil.

<sup>&</sup>lt;sup>1</sup> S. J. Allen, PHYS. REV., XXVII., p. 294, October, 1908.

A wire was next exposed to radium emanation and the absorption curve obtained as before. The characteristic inflection reappeared. It is not quite so marked as in the case of the atmospheric curve but it is evident that part, if not all, of the easily absorbed radiation comes from radium excited activity.

Four curves were then obtained which were so timed that the inflection point should come at 30, 50, 60 and 140 minutes from the time of discharge of the wire. The point of inflection is most marked in the first, less so in the second, still less in the third and does not appear at all in the fourth. Radium A has all transformed before the beginning of the observations, *i. e.*, in about ten minutes. The activity after about two hours is almost entirely due to radium C. The easily absorbed radiation cannot then be due to either of these and must therefore be due to radium B.

An effort was then made to measure directly the range of this radiation. Two methods of attack at once present themselves. The slit or bundle of tubes necessary to get rid of all except the normal rays may be dispensed with, since the distances used are so

very small. Or the pressure of the gas in which the  $\alpha$ -rays travel may be reduced to about one tenth atmosphere, when the distances will become large enough for the usual method. The first method was used for two reasons. First, apparatus was at hand with only slight alteration and, second, the radium bromide at present available is so weak as to make it desirable to utilize all the radiation possible. The results give justification for the first method. The apparatus is shown in section in Fig. 10 and does not differ from the ordinary form, used for these measurements, except in two points. First, as has been said, the bundle of tubes limiting the rays which reach the ion-trap to

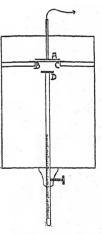


Fig. 10.

those shot off normally, was dispensed with. Secondly, a sheet of very thin aluminium foil (B-C, Fig. 10) was stretched tightly just below the plate A, connected with the electrometer. This sheet of foil was equivalent to about 0.5 mm. of air. It prevents the

diffusion of ions from below and at the same time lets through more  $\alpha$ -particles than a wire gauze. The plate A was set as close to the aluminium foil as possible without increasing the capacity of the system so much as to cause a large decrease in sensitiveness. The final distance used was about 7 mm. The plate was about 8

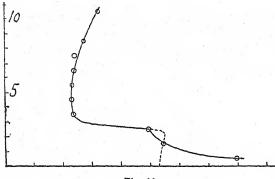


Fig. 11.

cm. in diameter. It is necessary to stretch the aluminium foil tightly as otherwise the attraction between the charged surfaces causes an alteration of the position of the aluminium foil.

The experimental curves obtained, as the distance of the wire, placed on the Table D, below the aluminium foil, was altered, are

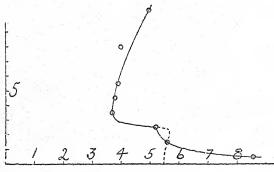


Fig. 12.

of the characteristic shape of those showing the range of  $\alpha$ -particles, except at the very lower part (see Figs. 11 and 12). The cause of the departure from the usual, dotted form, is easily explained.

Theory requires that the ion-trap shall be shallow in comparison with the range of the  $\alpha$ -particles. This is realized for the upper part of the curve where the  $\alpha$ -particles from radium C produce the ionization. Hence the curve takes the usual form for this part, and for the part where the short range particles just begin to reach the ion-trap. As the distance is further diminished however the short range particles produce more and more ionization. When the wire touches the aluminium foil they run their full range and hence produce the greatest ionization. The figures show that the easily absorbed radiation has a range between 2.6 and 3.0 mm. in air under normal conditions. The curves are plotted from the following data, corrected for the natural decay of the active material, and for the absorption by the thin sheet of aluminium foil.

Distance in mm. Ionization	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	8.0	8.5	10.5
Fig. 11.	800	545	495	267	260	263	290	290		325	375
Fig. 12.	860	560	520	360	370	380			400		500

#### SUMMARY.

- I. The half period of decay is not constant but varies from thirty minutes to five and a half hours.
- 2. Agreement between the experimental results and those calculated on the basis of a mixture of thorium and radium products is closer than the limit of experimental error.
- 3. The percentage of thorium excited activity for an equilibrium mixture varies between 10.6 and 76.0 per cent. of the total.
- 4. Percentages of thorium excited activity depend upon the following conditions: (a) A wire exposed at a low potential, 500 volts, collects a much larger percentage than one exposed at a high potential, 5,000 volts or over. (b) The percentage is very sensitive to barometric change. (c) The west wind is accompanied by the largest percentage, indicating that the air over the Pacific Ocean, off San Francisco, contains thorium emanation or that the tidal marshes over which the wind comes have an unusually high percentage of thorium salts.
- 5. The greatest amount of active material is collected on days when there is a north wind.

- 6. Variation in atmospheric pressure and not actual barometric height affects the amount collected.
- 7. Curves which have initially a convex upward part are obtained when an exposure is made while the barometer is rising.
- 8. The active deposit obtained at Denver, Colorado, does not differ appreciably from that obtained at Berkeley, California.
- 9. Results on the range of the  $\alpha$ -particles from the active deposit are in agreement with those obtained by S. J. Allen for the long range rays.
- 10. The short range  $\alpha$ -particles given off by the active deposit are due mainly if not entirely to radium B.
- 11. Nearly half the ionization produced by the deposit obtained from an open-air exposure is due to  $\alpha$ -rays which have a range of between 2.7 and 3 mm. in air, under ordinary conditions of temperature and pressure.

In conclusion I wish to thank Professor E. P. Lewis for his unfailing interest and kindness during the course of my investigations.

University of California,

November 15, 1908.

#### TELEPHONE RECEIVER IMPEDANCE.

By Roy T. Wells.

SEVERAL investigations have been made on the variation of the sensibility of the telephone receiver with the frequency of the current flowing in it. Rayleigh 1 and Wien 2 examined telephones with regard to their current sensibility, measuring the least current that would produce audible sound at different frequencies, and Austin 3 with regard to the volt sensibility, measuring the least impressed electro-motive force that would produce audible sound at different frequencies. A curve of either sort can be converted into one of the other if the impedance of the telephone at the different frequencies is known. Austin in his paper gave the resistance and inductance at 100 and 900 cycles per second.

Since a critical study of the telephone offers one of the promising fields for wireless telegraph development, it has seemed worth while to examine more carefully the variation of resistance, inductance and impedance with frequency.

The method used was to measure the resistance and inductance directly and at the same time by the Maxwell bridge method, as used by the writer in earlier work.<sup>4</sup> No attempt was made to develop the mathematical theory, which would be very complicated. The results, however, might be expected to, and do, agree in a general way with those found theoretically and experimentally for a long solenoid enclosing a conducting core, in the paper by the writer referred to above.

A variable standard of inductance was loaned by Prof. A. G. Webster, of Clark University, and Prof. W. L. Hooper, of Tufts College, opened his laboratory for the work, providing power and

<sup>&</sup>lt;sup>1</sup>Philosophical Magazine, 38, p. 294, 1894.

<sup>&</sup>lt;sup>2</sup> Annalen der Physik, 4, p. 450, 1901.

<sup>&</sup>lt;sup>3</sup> Bulletin of the Bureau of Standards, Vol. 5, No. 1, p. 153, 1908.

<sup>&</sup>lt;sup>4</sup> Physical Review, Vol. 26, No. 5, p. 337, 1908.

other apparatus. Mr. Munro, of Tufts College, was of great assistance in the work. The current supply was taken from a motor-driven alternator, giving any frequency up 1,000 cycles per second.

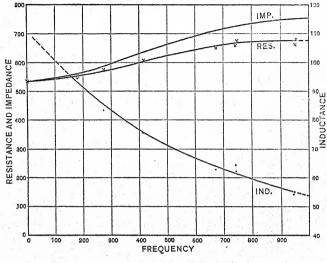
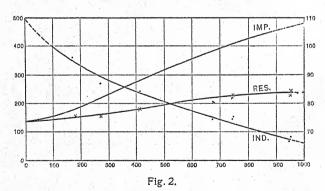


Fig. 1.

Two telephones were examined in detail. No. I was one of a pair of head telephones made for use as a wireless telegraph receiver. Its direct-current resistance was 531.6 ohms. No. 2 was a watch



case receiver, picked out at random in the Tufts College apparatus room. Its direct-current resistance was 132.2 ohms. Measurements made are given in Table I., the columns being headed f, R

and L, which signify respectively frequency in cycles per second, resistance in ohms and inductance in milli-henrys.

TABLE I.

£	No	. I.	No. 2.				
 	R	L	R	L			
0	531.6		132.2				
180	550	94.3	155	95.0			
274	575	83.3	155	87.0			
415	605	75.2	180	84.0			
674	650	63.0	205	74.5			
745	665	62.0	220	74.5			
748	675	64.5	230	75.2			
950	665	54.5	230	67.0			
954	680	55.0	245	68.0			

TABLE II.

	No	). I.	No. 2.			
ſ	R	L	Z	R	L	Z
0	531.6		531.6	132.2		132.2
50	534	105.3	535.0	137	103.8	140.8
100	539	100.4	542.7	140	99.4	153.3
150	545	95.6	552.4	144	96.0	170.1
200	553	91.2	564.7	150	93.0	190.1
250	562	87.1	578.4	156	90.4	210.9
300	573	83.3	594.2	163	88.0	232.6
350	586	79.7	611.6	170	85.8	254.0
400	598	76.5	628.3	178	84.0	276.1
450	610	73.6	644.5	185	82.3	297.3
500	621	71.0	659.8	193	80.7	318.7
550	632	68.8	675.2	202	79.0	339.6
600	643	66.8	690.5	209	77.4	358.9
650	653	64.8	704.6	215	75.9	377.2
700	660	62.9	715.6	221	74.4	395.4
750	667	61.2	726.6	226	73.0	411.8
800	671	59.5	734.6	231	71.6	427.6
850	673	58.0	740.8	234	70.2	441.9
900	675	56.5	746.8	237	68.8	455.6
950	675	55.2	751.0	240	67.5	469.0
1000	675	53.9	755.4	241	66.2	480.8

From this table the resistance and inductance curves of Figs. I and 2 were plotted, Figs. I and 2 applying to telephones nos. I

and 2 respectively. From the curves the values of resistance and inductance at frequencies up to 1,000 cycles per second by steps of 50 cycles were taken, and from the values the impedance Z was calculated in ohms. The results are given in Table II. and the impedance curves plotted in Figs. 1 and 2.

It will be noticed that the resistance and inductance tend toward a limiting value, while the impedance of course will increase indefinitely with the frequency.

### **PROCEEDINGS**

OF THE

## AMERICAN PHYSICAL SOCIETY.

Note on Spherical Aberration.1

By W. S. FRANKLIN.

THERE is much confusion at present in the terminology which relates to spherical aberration, and the publication of the interesting photograph, Fig. 1, gives an opportunity for calling attention thereto.

It would be seem to be desirable to use the general term spherical aberration for all those imperfections of a lens which lead to the production of non-spherical wave fronts. A very narrow pencil of rays passing through a lens parallel to the axis of the lens is not subject to spherical aberration because in the first place the transmitted waves are symmetrical

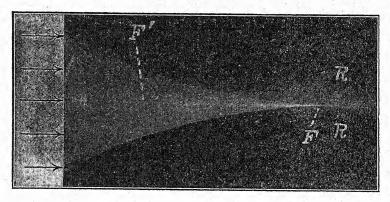


Fig. 1.

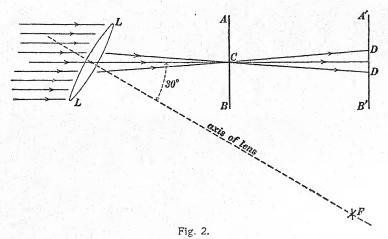
about the axis (equal curvature in every direction), and in the second place the transmitted waves are so small that they cannot be distinguished from sectors of a spherical surface. A broad beam of rays, however, is

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

subject to spherical aberration when it passes through a lens parallel to the axis of the lens. A narrow pencil of rays which passes obliquely through a lens becomes a well-defined astigmatic pencil, and a broad oblique pencil or beam of rays is very greatly confused by a simple lens.

There are, therefore, three kinds of spherical aberration, namely, (a) spherical aberration of a broad pencil of rays which emanates from a point in the axis of the lens, (b) spherical aberration of a narrow oblique pencil of rays, and (c) spherical aberration of a broad oblique pencil or beam of rays. The first is called axial spherical aberration, the second is called astigmatism, and the third is called oblique spherical aberration, or coma.

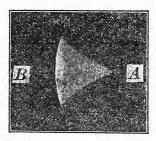
The character of axial spherical aberration is beautifully shown by the accompanying Fig. 1. A broad beam of parallel rays passes through a moderately short-focus plano-convex lens, as indicated by the sketch lines in the figure, the region behind the lens is filled with smoke, and a



photograph of this illuminated smoke is taken. Ordinarily the caustic of a mirror or lens is thought of as a single surface, that is, a surface having a single sheet. As a matter of fact, however, a caustic surface is, in general, a surface of two sheets inasmuch as a wave front has generally two radii of curvature at each point. When a wave front is a surface of revolution one sheet of the caustic surface reduces to a line (the axis of revolution). Thus, in Fig. 1, the curved outline of the beam is one sheet of the caustic surface, and the brilliant line of light along the axis is the other "sheet" of the caustic surface. This brilliant line of light is formed by the focusing of the light at different distances from the lens by the different zones of the lens.

Fig. 2 shows, exactly one quarter size, a lens LL set obliquely to a

beam of parallel rays, and Figs. 3a and 3b show the spots of light which are produced upon photographic plates placed at AB and A'B', respectively, in Fig. 2. The sharp distinction between astigmatism (that is, sspherical aberration of a narrow oblique pencil) and coma may b



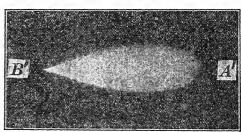


Fig. 3a.

Fig. 3b.

hown in a very striking way by covering the lens LL in Fig. 2 by ae cardboard with a small hole at its center, when the spots of light shown in Figs. 3a and 3b reduce to the two sharply-defined lines CC and DD in Figs. 4a and 4b.

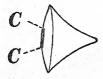
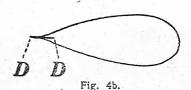


Fig. 4a.



THE THEORY OF COUPLED CIRCUITS.1

By Louis Cohen.

VITHIN the last few years several eminent physicists have made valuable contributions to the discussion of the theory of coupled circuits, but to my knowledge none of them succeeded in giving the complete solution of the problem. They had to resort to some method of approximation in one form or another.

The main difficulty involved in the solution of this problem is that it is necessary to obtain the four roots of a biquadratic equation. Theoretically, it is of course possible to do so, but practically the task is rather difficult, particularly so in this case where it happens that the various coefficients are complicated functions of the constants of the circuits.

I have succeeded in developing a method which enables me to avoid

<sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

this difficulty entirely. In place of the biquadratic, I can reduce the problem to two simple quadratic equations. Furthermore, all previous investigators limited themselves to the discussion of the case of electromagnetic coupling, and the case of direct coupling has been ignored entirely. My method, however, enables me to obtain the complete solution of both cases.

The work involved in the development of the theory is necessarily complicated, and it will not be possible to give in an abstract even an outline of the method adopted, so I shall merely limit myself in giving the final results obtained.

If we designate by  $V_1$  and  $V_2$  the potentials at any instant in the primary and secondary circuits respectively, then we shall have for the case of electromagnetic coupled circuits

$$\begin{split} V_1 &= \{H_1 e^{-\alpha_1 t} - H_3 e^{-\alpha_2 t}\} \cos \lambda_1 t + \{H_2 e^{-\alpha_1 t} - H_4 e^{-\alpha_2 t}\} \cos \lambda_2 t, \\ V_2 &= H_5 \{e^{-\alpha_1 t} - e^{-\alpha_2 t}\} \cos \lambda_2 t + H_6 \{e^{-\alpha_1 t} - e^{-\alpha_2 t}\} \cos \lambda_2 t. \end{split}$$

The constants  $H_1$  to  $H_6$  are somewhat complicated functions of the constants of the circuits and their values will be given in the complete paper which will soon be published. The values of the damping factors are as follows:

$$\begin{split} a &= \frac{L_2 R_1 + L_1 R_2 - \sqrt{(L_2 R_1 - L_1 R_2)^2 + 4 R_1 R_2 M^2}}{4 (L_1 L_2 - M^2)}, \\ \beta &= \frac{L_2 R_1 + L_1 R_2 + \sqrt{(L_2 R_1 - L_1 R_2)^2 + 4 R_1 R_2 M^2}}{4 (L_1 L_2 - M^2)}. \end{split}$$

 $\lambda_1$  and  $\lambda_2$  are the frequency constants and their values are given by the following equations:

$$\lambda_{1} = \sqrt{\frac{2(a_{1}a_{2} - d_{1}d_{2})a^{2} + (a_{2}b_{1} + a_{1}b_{2})a + (a_{1} + a_{2})}{2(a_{1}a_{2} + d_{1}d_{2}(b_{1} + b_{2})a - 2)^{2} + 2\{(a_{2}b_{1} - a_{1}b_{2})^{2} + d_{1}d_{2}(b_{1} - b_{2})^{2}\}a^{2}}}$$

$$= \sqrt{\frac{2(a_{1}a_{2} - d_{1}d_{2})}{2(a_{1}a_{2} - d_{1}d_{2})}}$$

$$\lambda_{2} = \sqrt{\frac{-\sqrt{d_{1}d_{2}}\{(b_{1} + b_{2})a - 2\}^{2} + 2\{(a_{2}b_{1} - a_{1}b_{2})^{2} + d_{1}d_{2}(b_{1} - b_{2})^{2}\}a^{2}}}{2(a_{1}a_{2} - d_{1}d_{2})}}$$

The various letters used have the following significance:

$$a_1 = L_1C_1, b_1 = R_1C_1, d_1 = MC_2$$
  
 $a_2 = L_2C_2, b_2 = R_2C_2, d_2 = MC_1$ 

where  $L_1$ ,  $R_1$ ,  $C_1$  and  $L_2$ ,  $R_2$ ,  $C_2$  are the inductance resistance and capacity of the primary and secondary respectively, and M is the mutual inductance.

For the case of direct coupled circuits, we have:

$$V_1 = \{ D_1 \cos \lambda_1 t + D_2 \cos \lambda_2 t \} e^{-at}$$

$$V_2 = \{ F_1 \cos \lambda_1 t + F_2 \cos \lambda_2 t \} e^{-at}$$

where

$$\lambda_{1} = \sqrt{\frac{L_{1}}{L_{1} + L_{2}}} a^{2} - R_{2}C_{2}a + 2$$

$$+ \sqrt{\frac{L_{1}}{L_{1} + L_{2}}} (R_{2}C_{2}a - 2)^{2} + \frac{L_{2}}{L_{1} + L_{2}} R_{2}^{2}C_{2}^{3}a^{2}$$

$$+ 2L_{1}C_{1}\frac{L_{2}}{L_{1} + L_{2}}$$

$$2L_{1}C_{1}\frac{L_{2}}{L_{1} + L_{2}}$$

$$\lambda_{2} = \sqrt{\frac{L_{1}}{L_{1} + L_{2}}} a^{2} - R_{2}C_{2}a + 2$$

$$- \sqrt{\frac{L_{1}}{L_{1} + L_{2}}} (R_{2}C_{2}a - 2)^{2} + \frac{L_{2}}{L_{1} + L_{2}} R_{2}^{2}C_{2}^{2}a^{2}}$$

$$+ 2L_{1}C_{1}\frac{L_{2}}{L_{1} + L_{2}}$$

$$a = \frac{R_{2}}{2L_{1}}$$

The constants of course have the same meaning as given above.

The expressions for the currents in the circuits can be derived from the potentials, and they are given in the complete paper.

Washington, D. C.

## Entladungsstrahlen.1

#### BY ELIZABETH R. LAIRD.

In 1895 Wiedemann and Schmidt, and in 1897 Hoffman published work describing a particular effect in the neighborhood of the spark at atmospheric pressure which they ascribed to a kind of radiation named by Wiedemann "Entladungsstrahlen." The effect was that certain substances were made thermoluminescent by this means under conditions in which they could not be made so by exposure to light. Later J. J. Thomson showed that this radiation would ionize the gas through which it passed.

Some time ago the writer while at the Cavendish Laboratory confirmed one of Hoffman's results showing that at a pressure of a millimeter or two radiation comes from a spark capable of traversing two layers of paper and affecting a photographic plate and that a quartz plate or metal objects are opaque to it. At the same time attempts were made by the electrical

<sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

method to see if any of the radiation would be transmitted through thin aluminum, but with negative results.

Later an electrical effect was sought through thin aluminum at somewhat reduced pressures, with negative results also except when the connections were such hat the aluminum was covered with a faint glow on the side opposite the ionization chamber.

The present work includes the repetition of a number of Hoffmann's experiments and was undertaken since the question has been raised as to whether these rays differ from ordinary light rays or from ions. thermoluminescent method of detection was chosen, and a solid salt solution of calcium sulphate + 2 per cent. manganese sulphate was used for the purpose. According to Hoffman when this is heated it loses its power of becoming thermoluminescent when exposed to light, but regains it when exposed to the spark. This, after some trials with different samples of salt, was confirmed, and a piece of quartz used as test during the course of the experiments always acted as an opaque object. The arrangements for observing the thermoluminescence were similar to those used by Hoffmann, a small radioscope was used to test the sensitiveness of the eyes before observations. In the greater number of experiments the salt was deposited on mica instead of on copper, as used by Hoffmann, to avoid chance electrical disturbances due to the metal.

When a small Wimshurst machine was used about double the capacity of the small Leyden jars forming a part of it had to be used to obtain a marked effect. If pointed electrodes were used instead of rounded ones the salt had to be placed nearer to obtain the same effect, and in this case no thermoluminescence was observed unless some capacity was used. This agrees in general with Hoffmann's observations and would show that the radiation from some forms of discharge is more easily absorbed or less in quantity, and also that the effect is not due to slow moving ions.

To test this further an air current was passed over the surface of the salt at right angles to and below the spark of an induction coil. When the salt was heated the shadow of the tube from which the air current came could be plainly seen, but no diminution in intensity could be observed in its path, although the speed at the outlet computed from the amount of air used was over 200 cm./sec.

A magnetic deflection was sought by Hoffmann and not found. A different method used here gave the same result. A number of experiments were made. In one a magnetic field estimated at 8,000 C.G.S. units was used. The spark from a Holtz-machine was the source, and was at right angles to and above the poles of the electromagnet. Below the spark and just above the poles was a slit made in a piece of mica, below the poles was the salt. A strip on the salt was exposed with the magnetic field on. The salt was then moved parallel to the magnetic

field and a similar strip exposed with the current off. The salt was then heated and the two bands of light compared. One edge was especially sharp, and no displacement of one relative to the other was observed, also the distribution of light in the two corresponded closely. The radiation had to traverse this field a distance of over 2 cm. Any ions of cathode ray magnitude would have been deflected, or if of atomic magnitude unless moving with velocities over 10<sup>8</sup> cm./sec.

The absorption of the radiation in air was observed especially with the spark of the induction coil as source. At a distance of 1.5 cm. the thermoluminescence was bright, at 4 cm. for the same time of exposure none at all was observed, and with three times the exposure, at a distance of 2.5 cm., the brightness was not over half the original, although an inverse square law would make these about equal. A current of impure oxygen from a gas cylinder passed over the salt while it was being exposed to the spark did not diminish the brightness especially. The effect of carbon dioxide was studied by placing the salt in a glass dish, the cover of which contained a slit and which was partly filled with solid carbon dioxide. When the distance of the salt below the cover was about 4 cm. and from the spark of the Holtz machine about 6 cm., a diminution in brightness was observed, so that increasing the time of exposure one half did not give quite as bright thermoluminescence as obtained with air at the same distance and for the same time of exposure. These experiments with carbon dioxide were repeated on three different days, in all seven times, and with the same general result which differs greatly from that obtained by Hoffmann.

When the salt was deposited on copper, it was noted that, when the induction coil was used, the greater thermoluminescence was on the side of the anode. This was traced to a projecting point on this side which slanted down somewhat towards the salt and was covered with a glow of light. A similar effect was obtained by curving the German silver wire forming the electrode downwards. If the current in the coil were reversed no special effect was noted under the projecting point, it was also absent when the salt was deposited on mica. This seemed to indicate that it might be due to the metal acting partly as cathode. It was found also that if a hissing discharge from the Wimshurst machine passed directly to the plate the greater thermoluminescence was on the side towards the positive electrode.

Thermoluminescent effects similar to those obtained in the above experiments followed if the salt were placed under a bend in a wire inserted in the secondary of the induction coil on either the positive or negative side of the spark gap, this effect was likewise cut off by quartz. No appreciable effect was obtained from a thin strip of aluminum inserted in a circuit consisting of a short spark gap and Leyden jar charged from the induction coil, but the power used was small.

These experiments tend to confirm the existence of something coming from the spark other than light or slow moving ions, which is not readily deflected, if deflected at all, in a magnetic field, which is absorbed by air and to a somewhat greater extent by carbon dioxide, and which may be called Entladungsstrahlen.

# Magnetic Double Refraction Normal to the Field in Liquids.<sup>1</sup>

By C. A. SKINNER.

OTTON and Mouton<sup>2</sup> discovered recently that nitrobenzol when placed in a magnetic field becomes double refracting in a direction normal to the field, and that this property follows Kerr's law for double refraction in an electric field. They found also that the dispersion in the two fields is the same within an accuracy of measurement of two per cent. in the violet and ten per cent. in the red region of the spectrum.

Possessing in the Brace half shade elliptic polarizer a very sensitive means of measuring double refraction of this kind; and the results o McComb,<sup>3</sup> who has been making an extensive study of electric double refraction of liquids in this laboratory, I have been led to investigate electric double refracting liquids in general for the presence of corresponding magnetic double refraction.

Of fourteen liquids thus far investigated, eight show a measurable relative retardation of the vibration perpendicular to the field (as compared with that parallel to it) in both electric and magnetic fields; two show a relative retardation of the parallel component in both; one, a relative retardation of the perpendicular component in the electric field, and of the parallel in the magnetic; one a measurable effect in the electric, but nothing observable in the magnetic field; and two show the effect in the magnetic, but nothing observable in the electric. Of these, nine have been compared for dispersion, showing without exception that this is the same in the two fields.

Kerr's law for electric double refraction may be stated thus:

$$\delta_e = B_e E^2 l$$

in which  $\delta_e$  = number of waves of the perpendicular vibration minus number of waves of the parallel vibration in a length of I centimeters of the liquid normal to the electric field of intensity E electrostatic units.  $B_e$  = the value which  $\delta_e$  takes for unit length of path in unit field.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Baltimore meeting of the Physical Society, December 28-31, 1908.

<sup>&</sup>lt;sup>2</sup> Compt. Rend., July, 1908.

<sup>3</sup> See abstract of paper in PHYS. REV., Sept., 1908.

The corresponding law for magnetic double refraction is

$$\delta_m = B_m H^2 l$$

in which H is the intensity of the magnetic field in C.G.S. units.

The following table is a brief summary of the results obtained with a tube of liquid 6 cm. long in a magnetic field of about 14,000 C.G.S. units. The values of  $B_e$  were furnished by Mr. McComb.

	$B_m$ ( $\lambda = 500$ )	$B_m/B_e$ (for all values of $\lambda$ )
Nitro benzol	$34 \times 10^{-13}$	$1.06 \times 10^{-7}$
Nitro toluol	21	1.61
Chlor benzol	11.4	8.3
Brom benzol	10.5	8.8
Benzol	9.0	176
Di ethyl aniline	6.8	4.9
Di methyl aniline	9.7	8.1
a-naphthalene bromide	33	30
Carbon bisulphide	<b>—5.3</b>	12.8

It appears rather remarkable that although carbon bisulphide shows a different component to be relatively retarded in the magnetic field to that in the electric yet the ratio  $B_{\rm m}/B_{\rm e}$  is, within the limits of experimental accuracy, the same for all wave-lengths ranging from 440 to  $660 \times 10^{-7}$  cm.

The question as to how accurately the double refraction is proportional to the square of the strength of the magnetic field has not as yet been thoroughly investigated.

THE BRACE LABORATORY OF PHYSICS, UNIVERSITY OF NEBRASKA.

#### NEW BOOKS.

Experimental Elasticity. By G. F. C. SEARLE. Cambridge Physical Series, 187. Pp. xvi. G. P. Putnam & Sons, 1908.

There is perhaps no topic in mechanics more difficult for the average student than elasticity, and yet none of more vital importance in all practical applications. As a rule, authors either make the treatment almost meaningless by the assumption of all formulæ without any notion of their physical basis, or else plunge the student into a maze of mathematical symbols both confusing and devoid of physical interest. It is consequently refreshing to have a book at once physical in spirit and yet using to advantage such mathematical tools as the student should be expected to possess at the stage represented by this work.

The first portion of the book contains a discussion of elementary principles, of elastic constants and their relations, including the relation between adiabatic and isothermal expansions. This is followed by the "solution of some simple elastic problems," which are quite suggestive of methods useful in more complex cases. Then follows a laboratory course of fourteen experiments very clearly stated and with perhaps an overabundance of suggestion.

Several related topics are treated in the "notes" which constitute a large part of the book. Note X, on "laboratory work," may be read with profit by any student or teacher.

J. S. SHEARER.

Refrigeration. An Elementary Text-book. By J. W. Anderson. Pp. ix + 242. Longmans, Green & Co., 1908.

The rapid development of practical refrigeration has created a demand for books dealing in a general way with this topic. This volume is a rather popular presentation of the elements of refrigeration theory and practice. The first fifty pages contain a review of elementary heat such as is found in most text-books. Then follows a discussion of the construction and installation of refrigerating machinery and of the special applications now common. Details relate almost entirely to English practice which will not increase the value to American readers.

The use of both English and metric units is unfortunate in a book of this kind as it is often confusing and serves no useful purpose. The problems which are solved in the text will be of considerable assistance to the non-technical reader. Electrical Engineer's Pocket-Book. Fifth Edition. By HORATIO A. FOSTER. Pp. xxxvi + 1599. New York, D. Van Nostrand Company, 1908.

This new edition, containing 600 pages more than previous editions, is practically a new book; in all parts the revision has been complete. The amount of information given in condensed form is simply enormous, and certainly the compiler deserves the thanks of all who use the book for making the information so readily available.

During the last year we have been given two excellent hand-books; as in the case of two telephone systems, each one no doubt is better on account of the other. In the case of these hand-books, each serves to supplement and to check the other. Any worker in electricity needs one handy; and the other somewhere accessible.

It is open to question whether the term "practical unit" should be applied to any unit which does not belong to the "practical system." The Gauss and Maxwell, for example, are names applied to certain C.G.S. units. These are not units of the practical system; neither is the kilowatt. The term "practical," when applied to these units, is used in a popular rather than a technical sense. It seems unfortunate to longer preserve the term static transformer, the adjective being unnecessary and even misleading.

F. B.

Illustrated Technical Dictionary in Six Languages: English, German, Russian, Italian, Spanish. Edited by K. Deinhardt and A. Schlomann, Vol. II.: Electrical Engineering. Compiled by Chas. Kinzbrunner. Pp. xii + 2100. Munich and Berlin, R. Oldenbourg; New York, McGraw Publishing Co., 1908.

The scheme of this dictionary and its execution are both excellent. A topical rather than alphabetical arrangement is employed, bringing together all words pertaining to one subject; a finding index is appended. The illustrations, of which there are about 4,000, add materially to the value of the book. The work has been prepared by a permanent staff, over thirty in number, assisted by several hundred co-operators.

Electro-Metallurgy. By John B. C. Kershaw. Pp. xv + 303. New York, D. Van Nostrand Company, 1908.

With no attempt at discussing theory, the author gives a clear account of the manufacture of aluminum, bullion and gold, calcium carbide and acetylene gas, carborundum, copper ferro-alloys, glass and quartz glass, graphite, iron and steel, lead, miscellaneous products, nickel, sodium, tin and zinc.

The processes are adequately described in a manner that can be understood by those whose acquaintance with either chemical or electrical

science may be but slight. The author has collected much valuable information in this rapidly developing field.

The Theory, Design and Construction of Induction Coils. By H. Armagnat. Translated and edited by O. A. Kenyon. Pp. v + 216. New York, McGraw Publishing Company, 1908.

With the increased use of the induction coil in wireless telegraphy, electrotherapeutics, gas-engine ignition, etc., there is an increased demand for exact knowledge concerning it; this demand is well met in the present book. A good description is given of various forms of interrupters, and a full discussion of the theory of mechanical and electrolytic interrupters. The bibliography — to which the translator has added — is particularly valuable, containing 104 references, many of which are briefly abstracted. The translator and the publishers have succeeded in producing an attractive edition of this little book.

Electric Lighting and Power Distribution. By W. P. MAYCOCK. Vol. I. Seventh Edition. Pp. xix + 599. London, Whittaker & Co., 1908.

This is an elementary book, intended particularly for English students preparing for the examinations of the City and Guilds of London Institute. It is clearly written and deals in a satisfactory manner with the elementary laws of electricity and magnetism, and with measuring instruments, but — save for the discussion of the dynamo — scarcely touches the subject of lighting and power distribution, nor the subject of alternating currents. Presumably these topics are reserved for Vol. II. In this edition, the book has been much enlarged.

- The Principles of Alternating Currents. By Edgar T. Larner. Pp. viii + 136. New York, D. Van Nostrand Company, 1908. (Received.)
- Die elektrischen Eigenschaften und die Bedeutung des Selens für die Elektrotechnik. By Dr. Chr. Ries. Pp. i + 86. Berlin, Nikolassee, Administration der Fachzeitschrift, der Mechaniker, 1908. (Received.)
- Histoire du Developpement de La Chimie Depuis Lavoisier Jusqu'a Nos Jours. By A. Ladenburg. Traduit sur la 4° edition allemande by A. Corvisky. Librairie Scientifique, A. Hermann & Fils. 1909. (Received.)

#### THE

# PHYSICAL REVIEW.

COLLOIDAL SOLUTIONS, AND THE REFRACTIVE INDICES OF GOLD, PLATINUM AND SILVER.

By B. J. SPENCE.

#### Introduction.

DURING the last few decades, there have appeared from time to time articles dealing with the question of the optical properties of turbid media.

It will be seen from the brief abstracts of these papers which form the introduction to the present article, that the theoretical conclusions at which the various writers arrive seem to indicate that the transmission of light by a turbid medium should be a simple function of the period of the light.

The theories have been tested in a number of instances in the somewhat narrow range of wave-lengths comprising the visible spectrum, with the result that while some investigators have found agreement between theory and experiment, others have reported disagreement.

The object of the present investigation has been to supplement the existing data obtained in the visible spectrum by extending the field of investigation as far as possible into the infra-red region of the spectrum.

The pioneer work of a theoretical character is due to Lord Rayleigh, who deduced an expression for the light transmitted through an atmosphere containing small insulating particles in suspension. This was shown to depend on the number and size of

<sup>1</sup> Phil. Mag., XLI., 107, 1871; XII., 81, 1881.

the particles suspended in unit volume of the supporting medium. Lord Rayleigh 1 again took up the subject later, developing it more completely and obtained an expression for the energy transmitted as a function of the wave-length, index of refraction of the suspended particle, and the number of particles per unit volume, assuming that the particles were insulators and spherical in shape. The following formula is given by Lord Rayleigh

$$H = \frac{32\pi^3(\mu - 1)^2}{3N\lambda^4}$$

where H is given by the formula

$$E = E_0 e^{-Hd}$$
.

In these expressions  $\mu$  represents the refractive index of the suspended particle, N the number of particles per unit volume, d the thickness of the layer,  $E_0$  and E are the incident and transmitted energies respectively. The first equation leads to the important deduction that the absorption varies as the  $\lambda^{-4}$ , and the correctness of the theory in this respect may be readily determined, after H has been experimentally found for the various wave-lengths for the given turbid medium.

Lord Rayleigh has also found that light scattered by these insulating particles, and produced by the incidence of plane polarized light, vanishes at all points in a plane normal to the magnetic induction, where the radius vector makes an angle of 90° with the direction of the incident light.

The theory to explain the transmission of light by solutions or atmospheres composed of conducting particles has been developed by J. J. Thomson,<sup>2</sup> who finds that the scattered light produced by the incidence of plane polarized light, vanishes in a plane through the center at right angles to the magnetic induction in the incident wave, along a line making an angle of 120° with the radius to the point at which the wave first strikes the sphere, and it does not vanish in any other direction than this. This is quite a different conclusion from that arrived at by Lord Rayleigh in his analysis for insulating particles.

<sup>&</sup>lt;sup>1</sup>Phil. Mag., XXXXVII., 375, 1889.

<sup>&</sup>lt;sup>2</sup> Recent Researches, p. 437.

Ehrenhaft undertook an experimental test of Thomson's theory for media containing metallic particles in suspension, commonly known as colloidal solutions. For colloidal solutions of gold, silver, platinum and copper, he found the maximum of polarization to be at angles of 118°, 110°, 115° and 120° respectively with the incident energy. He also found that the amount of polarization varied directly as the amount of metal per unit volume of the supporting medium

Ehrenhaft in his investigation found that the colloidal solutions which he examined possessed strong absorption bands in the visible spectrum. The absorption band of gold colloid occurred at a wave-length of  $5.2 \times 10^{-5}$  cm., that of platinum at  $4.8 \times 10^{-5}$  cm., and that of silver at a wave-length  $3.8 \times 10^{-5}$  cm. According to Thomson it is possible from the position of these bands, due to optical resonance, to compute the order of magnitude of the size of the suspended particles.

Let t represent the period of vibration of the particle, v the velocity of propagation of the disturbance, and a the radius of the metal sphere, then

$$t = \frac{4\pi a}{\sqrt{3v}}.$$

If n be the refractive index of the supporting medium, then  $v = n/\lambda$  so that

$$a = \frac{\sqrt{3}}{4\pi} \frac{\lambda}{n}.$$

From the values of the wave-lengths at which resonance takes place, Ehrenhaft computed the size of the particles to be of the order of magnitude of  $40 \times 10^{-7}$  cm., and this magnitude falls within the limits assigned to it by Thomson.

Another piece of experimental work, similar to that of Ehrenhaft, is that of Müller,<sup>2</sup> who found the azimuth of polarization for platinum, silver and gold colloids to be 112°, 97.5°, 125°, respectively, and that for a medum consisting of insulating particles, the azimuth of polarization was less than 90°. These values for colloidal solu-

<sup>&</sup>lt;sup>1</sup> Sitz. ber. Akad., Wiss. Wien, 112, IIa., 1903.

<sup>&</sup>lt;sup>2</sup> Ann. der Physik, 24, 1, 1907.

tions of platinum, silver and gold do not accord with the results of Ehrenhaft, who found a better agreement between the experimental and theoretical values. Müller's results afford no explanation of the optical properties of colloidal solutions based on the size of the particles.

More recently Mie<sup>1</sup> has published a paper which deals with the turbid media, based on the assumption that the particles may be regarded as spherical in shape, and that the turbidity is infinitely thin, in an optical sense. The light emitted by a particle may be calculated as a series of partial waves of which there are two groups, corresponding respectively to the electric and magnetic vibrations of the particles. In a colloidal solution consisting of very small particles the first harmonic is small, and corresponds to the formula of Lord Rayleigh, which was previously discussed. For coarser particles other electric and magnetic harmonics appear.

Mie also found from theoretical considerations that the unpolarized ray on passing through a medium should be linearly and partially polarized. The light diffused by gold particles up to a size of  $I \times I0^{-5}$  cm. consists entirely of radiation corresponding to the Rayleigh formula, and the azimuth of polarization occurs at 90°. For particles from  $I.6 \times I0^{-5}$  cm. to  $I.8 \times I0^{-5}$  cm. in diameter the azimuth of polarization lies between  $II0^\circ$  and  $I20^\circ$ . These results, therefore, seem to account for the discrepancy between the results of Ehrenhaft and Müller, with regard to the azimuth of polarization, it being due merely to the different sizes of the particles which occur in colloidal solutions made under different conditions.

Mie's work also shows that the absorption of light by turbid media is proportional to the amount of metal per unit volume of the supporting medium, when the particles in suspension are small.

Garnett<sup>2</sup> has developed a theory, in which he has explained the optical properties of colloidal glasses, and since Garnett's work has been made the basis of the work contained in this paper, we shall give a brief resumé of his paper in so far as it will be necessary to make clear its bearing upon the present subject.

<sup>&</sup>lt;sup>1</sup> Ann. der Physik, 25, 377, 1908.

<sup>&</sup>lt;sup>2</sup> Phil. Trans., A., 204-205, 1905.

If light of a wave-length  $\lambda$  falls upon a metal sphere of radius  $\alpha$ , of refractive index n, and extinction coefficient k, then the complex dielectric constant  $\epsilon$  will be expressed by

$$N = n(\mathbf{I} - ik) = \sqrt{\varepsilon}.$$

Lord Rayleigh 1 has shown that a metal sphere of radius a, index of refraction n, and extinction coefficient k, when excited by an electric force  $E_0$ , emits the waves which would be emitted by a Hertzian doublet whose moment at a time t is

$$\frac{N^2 - 1}{N^2 + 2} a^3 E_0,$$

where  $N^2$  is the complex dielectric constant of the metal and equals  $n^2(1-ik)^2$ .

For the case in which there are a great many spheres close together the electric force for each doublet would be the force  $E_0$  together with that due to the neighboring doublets. Calling this E' then at any time t, the polarization is

$$f(t) = a^{3} \frac{N^{2} - 1}{N^{2} + 2} E'$$

which is regarded as the average moment. If m be the number of doublets present, then the polarization is expressed by

$$f'(t) = mf(t).$$

Lorentz and Larmor have shown that

$$E' = E_0 + \frac{4\pi f'}{3} = E_0 + \frac{4\pi}{3} ma^3 \frac{N^2 - 1}{N^2 + 2} E',$$

provided only that the doublets are scattered through a space large compared with the wave-length. Solving for E' and f, we obtain the expressions

$$E' = E_0 \left\{ \frac{I}{I - \frac{4\pi}{3} ma^3 \left[ \frac{N^2 - I}{N^2 + 2} \right]} \right\}, \tag{I}$$

$$f = \frac{E_0 \left[ \frac{N^2 - 1}{N^2 + 2} \right] a^3}{1 - \frac{4^{\pi}}{3} ma^3 \frac{N^2 - 1}{N^2 + 2}}.$$
 (1')

<sup>1</sup> Phil. Mag., XLIV., 28, 1897.

By the use of the Maxwell equations, the complex dielectric constant is expressed as

$$\varepsilon \frac{\partial E}{\partial t} = c \operatorname{curl}(H) \operatorname{and} \frac{\partial H}{\partial t} = -c \operatorname{curl}(E),$$

it follows

$$\varepsilon' = \frac{E + 4\pi f'}{E},$$

$$= \frac{1 + 4\pi ma^3 \left[ \frac{N^2 - 1}{N^2 + 2} \right]}{1 - \frac{4\pi ma^3}{3} \left[ \frac{N^2 - 1}{N^2 + 2} \right]}.$$

This shows that a medium consisting of small metallic spheres is optically equivalent to a medium of refractive index n', and extinction coefficient k', given by the expression

$$N' = n'(\mathbf{I} - ik') \equiv \sqrt{\varepsilon'},$$

in which

$$\varepsilon' = I + \frac{4\pi ma^3 \frac{N^2 - I}{N^2 + 2}}{I - \frac{4\pi ma^3}{3} \left[ \frac{N^2 - I}{N^2 + 2} \right]}.$$

This expression holds only for the case in which the metallic spheres are distributed in vacuo, many to the wave-length. If  $\mu$  represent the relative volume, then

$$\mu = \frac{4}{3}\pi ma^3$$

and the above equation becomes

$$\varepsilon = 1 + \frac{3\mu \frac{N^2 - 1}{N^2 + 2}}{1 + \mu \left[\frac{N^2 - 1}{N^2 + 2}\right]} = n'(1 - ik'). \tag{2}$$

This equation which is due to Garnett, forms the point of departure for the mathematical analysis of the special problem with which the present paper deals.

EXTENSION OF THE THEORY.

A colloidal solution may be regarded as one consisting of small spherical particles, as Siedentopf<sup>2</sup> and Zsigmondy have shown by

<sup>1</sup> Loc. cit.

<sup>&</sup>lt;sup>2</sup> Ann. der Physik, January, 1903.

means of the ultra microscope. Burton  $^1$  in his work upon electrically prepared colloidal solution has shown that the diameter of the particles in such solutions is of the order of magnitude of  $4 \times 10^{-5}$  cm. to  $6 \times 10^{-5}$  cm. This value is in accord with the values which Bredig  $^2$  found by theoretical considerations alone, Bredig shows that when these particles are viewed with a microscope of the highest power, the particles remain undetected, yet when a beam of light is passed through a solution containing them, the beam is scattered and polarized. The best microscopes can detect particles of the order of magnitude of  $14 \times 10^{-5}$  cm. and yet these particles since they diffuse light must be of the order of magnitude of a light wave, so that the lower limit to the size of the particle is  $10^{-5}$  cm.

From the work which has been done by these investigators it seems that we are justified in assuming that the magnitude of this particle is 10<sup>-5</sup> cm. as a lower limit, and so are at liberty to apply Garnett's analysis to the case of colloidal solution, for in them we are dealing with particles of approximately the same order of magnitude as those with which he had to deal in his work upon metal or colloidal glasses.

However, since it is impossible to prepare colloidal solutions in a medium which does not itself possess absorption in the infra-red spectrum, it has been found necessary for the purposes of the present investigation to extend Garnett's analysis to include the case of an absorbing medium whose complex dielectric constant is  $v(\mathbf{I}-ig)$ .

If now in equation (2) (which holds only for the case of spherical particles embedded in the æther) we replace the dielectric constant of the æther, unity, by the complex dielectric constant s'' = v(1 - ig) of the supporting medium. We obtain the following equation

$$\varepsilon' = \varepsilon'' + \frac{3\varepsilon''\mu \left[\frac{\varepsilon - \varepsilon''}{\varepsilon + 2\varepsilon''}\right]}{1 + \mu \left[\frac{\varepsilon - \varepsilon''}{\varepsilon + 2\varepsilon''}\right]} \cdot (2')^3$$

<sup>&</sup>lt;sup>1</sup> Phil. Mag., II., 1906, p. 425.

<sup>&</sup>lt;sup>2</sup> Drude's Ann., XI., 218, 1903.

<sup>&</sup>lt;sup>3</sup> The first term in the denominator of equation (2') is not a dielectric constant, but a pure number and hence is not replaced by  $\varepsilon''$ .

In the above equation we may neglect

$$\mu\left[\frac{\varepsilon-\varepsilon''}{\varepsilon+2\varepsilon''}\right]$$

with respect to unity since it is of the order of magnitude of 10<sup>-5</sup>, and we thus obtain the equation

$$\varepsilon' = 3\varepsilon''\mu \left[ \frac{\varepsilon - \varepsilon''}{\varepsilon + 2\varepsilon''} \right] + \varepsilon'', \tag{3}$$

where

$$\varepsilon = n^2 (1 - ik)^2,$$
  

$$\varepsilon' = n' (1 - ik')^2.$$

Equation (3) may be written in the form

$$\varepsilon' = \varepsilon'' \left( 1 + 3\mu \frac{\varepsilon - \varepsilon''}{\varepsilon + 2\varepsilon''} \right),$$

or it may be written

$$\frac{\varepsilon'}{\varepsilon''} - 1 = 3\mu \frac{\varepsilon - \varepsilon''}{\varepsilon + 2\varepsilon''} = \alpha + i\beta. \tag{4}$$

Replacing the values of  $\varepsilon$ ,  $\varepsilon'$  and  $\varepsilon''$  by their values in terms of refractive indices and extinction coefficients, we obtain for the second member of equation (4)

$$3i \quad \frac{n^2k^2 + v^2 + 2i(n^2k - v^2g)}{n^2k^2 - 2v^2 + 2i(n^2k - 2v^2g)} \right] = \alpha + i\beta.$$

Separating real and imaginary quantities we obtain for the value of  $\beta$ 

$$\beta = 6\mu \left[ \frac{(n^2k - v^2g)(n^2k^2 - 2v^2) - (n^2k + 2v^2g)(n^2k^2 + v^2)}{(n^2k^2 - 2v^2)^2 + (n^2k + 2v^2g)^2} \right]. \tag{5}$$

In the above equation g is of the order of magnitude of  $10^{-5}$ , and hence terms containing g may be neglected with respect to terms containing n and k alone, and the equation for  $\beta$  becomes

$$\beta = \frac{-18n^2kv^2\mu}{(n^2k^2 - 2v^2)^2 + n^4k^2}.$$
 (6)

The quantity k is an extinction coefficient and is not known, but

if we replace k by a/n, where a is the absorption coefficient of the metals and is quite accurately known from the work of Rubens <sup>1</sup> and Hagen, and n is the refractive index of the metals, we obtain an equation containing n and  $\beta$  as unknown quantities. Equation (6) then becomes

$$\beta = \frac{-18nav^2\mu}{(a^2 - 2v^2)^2 + n^2a^2}. (7)$$

It is necessary to find a value of  $\beta$  in terms of quantities which may be experimentally determined. This we may do by replacing the values of  $\varepsilon'$  and  $\varepsilon''$  by their values in terms of refractive indices and extinction coefficients in the first members of the equation (4) we obtain

$$\frac{\varepsilon'}{\varepsilon''} - \tau = \frac{\varepsilon' - \varepsilon''}{\varepsilon''} = \frac{n'^2 - v^2 - 2i(n'^2k' - v^2g)}{v^2 - 2iv^2g} = \alpha + i\beta.$$

If we equate real and imaginary quantities and collect imaginary quantities we obtain for  $\beta$  a value

$$\beta = 2 \left[ \frac{g(n'^2 - v^2) - (n'^2 k' - v^2 g)}{v^2 (1 + g^2)} \right].$$

If we make the approximation that in the range from a wavelength  $5.8 \times 10^{-5}$  cm. to  $6.8 \times 10^{-5}$  cm., the refractive index of the colloidal solutions differs only very slightly from the refractive index of the supporting medium we obtain by setting n' = v

$$\beta = -\frac{2v^2(k'-g')}{v^2} = 2(g-k').$$

This equation in terms of the extinction coefficients of the colloidal solution and the supporting medium may be transformed into one involving the absorption coefficients t and w by means of the relation k'n' = t and vg = w. Since we have assumed that n' = v, we obtain

$$\beta = -\frac{2(t-w)}{v}.\tag{8}$$

<sup>1</sup> Phil. Mag., 7, 1904.

Equating equation (7) and equation (8), we obtain

$$t - v = \frac{9nav^3\mu}{(a^2 - 2v^2) + n^2a^2}. (8')$$

Solving for n', we obtain

$$n = \frac{av^3}{2a(t - vv)} + \sqrt{\left(\frac{av^3}{2a(t - vv)}\right)^2 - \frac{(a^2 - 2v^2)^2}{a^2}}.$$
 (9)

If in equation (8) we neglect  $n^2a^2$  with respect to  $(a^2 - 2v^2)^2$ , which can be done only when the value of n is considerably less than unity, we obtain a very simple equation for n

$$n = \frac{(t - w)(a^2 - 2v^2)^2}{9av^3\mu}. (9')$$

Equation (9') may be used in computing the values of n for gold and silver for which the values of n known for the visible spectrum are much less than unity, but in computing the values of n for platinum equation (9) must be used owing to the fact that the values of n for platinum are much greater than unity in the visible spectrum.

We thus have arrived at an equation for the refractive indices of the metals, in terms of the absorption coefficients of the colloidal solution and of its supporting medium, the absorption coefficients of the metal forming the colloid, the refractive index of the supporting medium, and the relative volume of the metal present. The values of n for the three metals given by this method for the wave-length  $5.89 \times 10^{-5}$  cm. should agree fairly well with the values of n obtained by Drude <sup>1</sup> and Kundt, <sup>2</sup> for these metals at the wave-length  $5.89 \times 10^{-5}$  cm.

Several important deductions are immediately derived from equation (9'), first, if we neglect the absorption w due to the supporting medium, as Garnett did implicity in his analysis, we obtain an equation

$$n = \frac{t(a^2 - 2v^2)^2}{9av^3\mu}$$

<sup>&</sup>lt;sup>1</sup> Phys. Zeitschrift, January, 1900.

<sup>&</sup>lt;sup>2</sup> Wied. Ann., 34, p. 469, 1888.

which shows that t, the absorption of the colloidal solution, is proportional to the concentration  $\mu$ . Garnett arrived at an equation

$$\beta = \frac{n'k'}{3\mu v}$$

in which k'n' measured the absorption and  $\beta$  is a function of the optical constants of the metals, that is, n and k. This equation also shows that the absorption n'k' is proportional to the concentration.

If w be not neglected, we find from equation (9') that the difference between the absorption of the colloidal solution and the absorption of the supporting medium is directly proportional to the concentration.

Finally if n is to be an invariant for a given metal for a given wave-length, for any supporting medium, experimental determination of n should bring out the fact that n is independent of the supporting medium. The different supporting media in which small metallic particles will remain suspended long enough to admit of accurate observations are very few. However two supporting media were obtained which possessed widely different optical properties. The usual one, water, possesses very strong absorption bands in the range of wave-lengths from  $5.89 \times 10^{-5}$  cm. to  $15 \times 10^{-5}$  cm. and its general absorption is very large. The second supporting medium, ethyl malonate, is a complex organic compound, and possesses the usual bands due to the ethyl group. Its general absorption, however, is not so great as that of water, and it makes a much more desirable supporting medium owing to this fact.

The main results brought out of the above theoretical considerations are briefly these; first, the optical properties of colloidal solutions should be independent of the size of the particles, provided the diameter be small compared to the wave-length. We should thus expect to find the best argument between theory and experiment the longer the wave-length of light. Second, it should be possible to determine the optical constants of those metals, which may be brought into the colloidal state, by the determination of the difference between the absorption of the solution of known metal content and of the supporting medium; and the values so obtained should be independent of the nature of the supporting

medium. Third, the difference between the absorption of the colloidal solution and of the supporting medium should be directly proportional to the relative volume of the metal in the solution.

It will be seen further on that colloidal solutions of silver, gold and platinum exhibit optical properties which are in good agreement with these theoretical conclusions.

#### APPARATUS.

The investigation was carried on by means of a large spectro-bolometer of special construction designed by A. Trowbridge. The bolometer strips forming the two arms of the Wheatstone's bridge were 0.5 mm. wide and 2.5 cm. long. Their thickness may be judged from the fact that each of them had a resistance of 3 ohms. The remaining two arms of the bridge consisted of balancing coils, small portions of which were shunted by mercury sliders so that the balancing of the bridge was made very simple.

The bolometer strips were enclosed in an air-tight chamber through which the energy to be measured was allowed to enter through a rock-salt window.

The bolometer and its accessories were surrounded by a water jacket in order to protect the bolometer coils and sliders from irregular temperature fluctuations.

By means of a low power microscope mounted axially in the bolometer case it was possible to make accurately all preliminary adjustments for collimation, and to check the adjustments from time to time during the course of experimentation.

The spectrometer was provided with a divided circle graduated to minutes, on which settings were made with a micrometer microscope. The head of the micrometer screw was divided into sixty parts of such size that one tenth of a division could be readily estimated, thus allowing the observer to read with considerable accuracy to one tenth of a second of arc. The arms of the spectrometer were about one meter in length, and allowed the use of very long focus mirrors of considerable aperture.

The rock-salt prism used in the investigation had an angle of 60° 1′ 37″, was 12 cm. high, and had faces 7 cm. wide. It was mounted in a manner described by Wadsworth 1 in which the prism

faces and a mirror are so arranged that a plane bisecting the angle of the prism passes through the axis of the spectrometer table, and is also at right angles to the plane of the mirror, which plane passes through the axis of the spectrometer table. Employing this arrangement Langley 1 has shown that if the arms of the spectrometer are so fixed that the undeviated beam passing through from the slit into the collimator, arrives at and is focused on the bolometer strip, and then the prism arrangement inserted in the manner described above, the spectrum will arrive at the bolometer in such a way that light of any wave-length falling on the bolometer strip will have passed through the prism under minimum deviation.

The prism and mirror were mounted on a large circular casting of iron, which in turn was held upon the spectrometer by means of a hole, slot and plane device. The whole was then enclosed within a sheet-iron case with diaphragms in it for the entrance and exit of the beam.

The galvanometer was similar to that designed by C. E. Mendenhall and described by L. R. Ingersoll.<sup>2</sup> It was a four-coil astatic needle instrument, magnetically shielded by a triple concentric shield of exceptionally soft iron, kindly furnished by Mr. Elihu Thompson. A similar shield has been used for the past three years by Mendenhall and Trowbridge, who found that it reduced the field of the earth to one four-thousandth of its value outside the shield.

The coils had each a resistance of twelve ohms, and were connected in multiple so that their combined resistance was three ohms. The needle system was made of tungsten steel elements mounted in two groups, the whole weighing about six milligrams. As ordinarily used, with a period of about ten seconds, the sensibility of its galvanometer-bolometer arrangement was such that a candle at a distance of one meter gave about fifteen hundred scale divisions.

As a source of current for the bolometer, storage batteries at first were used, but considerable difficulty was encountered in their use, due to their irregular behavior. There are periods in the discharge of a storage cell which are fairly constant, but these periods are not of long duration, and just when they occur is a matter of uncertainty, owing to inconsistent conditions of charging and of previous state.

<sup>&</sup>lt;sup>1</sup> Annals of Smithsonian Institution, Vol. I.

<sup>&</sup>lt;sup>2</sup> Phil. Mag., 6, 61, p. 41, 1906.

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In order to obviate this difficulty, four large standard cells were made of a type which Professor G. A. Hulett 1 had been using for potentiometer work. Large battery jars which allowed a mercury surface of 340 cm.2 were used, and the wooden cover of each jar supported four anode cups, which contained the cadmium amalgam. These cups were 5 cm. in diameter. Since these cells were first constructed an improved form has been made, in which the anode cups were replaced by the rubber trays, supported by a glass frame resting upon the bottom of the jar. One and a half liters of acid cadmium sulphate solution, and 150 grams of mercurous sulphate were placed in each of these cells. The cells were then charged at a low current density. At first the charging was done without stirring, but later L-shaped stirrers were passed through the covers of the jars, and a much higher current density could be used without the danger of forming the basic salt. These cells were found to furnish a current of 0.2 ampere without the fluctuations experienced with the storage battery and with only a very slow drift. They are particularly well suited for bolometric work, for all the annoying features of the storage cell are removed.

The arrangement of the apparatus was as follows: A beam of light from a Nernst glower was allowed to fall upon a mirror, and was brought to focus upon the slit of the spectrometer. Before the slit was placed a sliding cell, containing the solution to be investigated. The energy from the slit was directed upon another mirror placed at such a distance from the slit, such that parallel light was reflected from it, and passed through the prism to another mirror of a meter focal length. This latter mirror brought to a focus upon the bolometer strip those rays which had passed through the prism under minimum deviation.

A simple and effective device was designed to carry the colloidal solution. Two quartz plates about 4 cm.² were separated by a hard rubber diaphragm, of known thickness. The rubber diaphragm was divided into two compartments. The plates and diaphragm were placed in a convenient cell and held in position by screws. The cell was made to slide on two brass ways so that either one of the compartments of the cell might be brought into the path of the rays

of light to the slit or removed entirely. The liquid to be investigated was placed in one of these compartments, the deflection of the galvanometer noted when energy of a known wave-length was transmitted through the compartment containing it, then the deflection was noted when energy passed through the empty compartment. Thus the effect of the absorption of the quartz could be eliminated from the observation and only the transmission of the liquid was obtained.

In order to know in exactly what part of the spectrum the observations were being made, it was necessary to obtain a dispersion curve of the rock-salt prism. In order to do this the angle of the prism was accurately measured, and from the known values of the dispersion of rock salt, determined by Rubens 1 and Trowbridge, a dispersion curve in terms of wave-lengths and angles of minimum deviation was obtained. This gave a simple and rapid means of determining the wave-length at which one was working provided the reading of the spectrometer was known at which energy of a known wave-length passed through the prism under minimum deviation. The accuracy of the method was tested by first setting on the sodium lines and then determining the angular reading. The setting for the emission band of CO<sub>2</sub> at  $44 \times 10^{-5}$  cm. was computed. A Bunsen burner was placed before the slit and a maximum of emission sought. It was found and the reading taken. This angular reading agreed with the computed reading to within less than I × 10<sup>-5</sup> cm. A device for roughly estimating the position of the infra-red spectrum at which observations were being made was obtained by placing a small concave mirror upon the case enclosing the prism, directly over the axis of the spectrometer table. A beam of light from a Nernst glower was focused upon a card-board fastened to the wall of the room. This was calibrated empirically for various wave-lengths.

#### EXPERIMENTAL.

The colloidal solutions employed were made according to the method of Burton.<sup>2</sup> Very stable colloids were obtained of gold,

<sup>&</sup>lt;sup>1</sup> Wied. Ann., 60, 724, 1897.

<sup>&</sup>lt;sup>2</sup> Phil. Mag., 11, 425, 1906.

platinum and silver. They remained in good condition almost indefinitely without coagulating or changing color.

Attempts were made to obtain colloids of the various metals in alcohol. In the cases of platinum, silver and gold the attempts were fruitless, owing to almost immediate precipitation. Lead, zinc and tin were tried and the resulting colloids appeared rough and granular. They began immediately to precipitate the metal, and in the course of a few days the entire metal content was precipitated. The constant change in the metal content made it impossible to obtain anything except a rough qualitative idea of the optical properties of these colloidal solutions.

The colloids of gold, platinum and silver which possessed a satisfactory stability were made in either water or ethyl malonate.

The amount of metal present per unit volume of supporting medium was readily and quite accurately determined by evaporating the colloidal solution to dryness, and weighing the residue. The weighings were made a number of times and the final error in the determination did not exceed three per cent. This method was also used by Burton.<sup>1</sup>

To determine the absorption coefficients of the colloidal solution and its supporting medium for any given wave-length, it was necessary to make use of two thicknesses of the cell. For if  $\lambda$  is the wave-length in vacuo, d the difference in thickness between the two layers of solution used, and  $I_1$  and  $I_2$  the incident and transmitted energies respectively, then the absorption k'n' is given by the expression

$$\frac{I_1}{I_2} = e^{-\frac{4\pi k'n'd}{\lambda}}.$$

Solving for k'n', we obtain

$$k'n' = \frac{\lambda}{4\pi d} \log \frac{I_2}{I_1} \frac{I}{\log e}.$$

All these quantities in the right-hand member of this equation are known or capable of experimental determination. The ratio  $I_2/I_1$  was determined by means of the bolometer, and d was measured by means of a micrometer caliper. The values of the absorption coef-

ficients for the various wave-lengths were determined for the various colloidal solutions and their supporting media.

### RESULTS.

Tables I., II. and III. contain the various quantities used in the determination of the values of the indices of refraction of the metal silver, for wave-lengths from 5.80  $\times$  10<sup>-5</sup> cm. to 15  $\times$  10<sup>-5</sup> cm. In the tables, columns 2 and 3 show the percentage of energy transmitted through the collodial solution for two different thicknesses of the solution. The difference in thickness of the two layers was 0.214 cm. Columns 4 and 5 show the ratio of the energy transmitted through the collodial solution to that transmitted through the supporting medium, which in the case of silver was water. Column 6 shows the values of the ratios from which the absorption coefficients of the colloidal solution were calculated. Column 7 shows the values of the absorption coefficients of the colloidal solution for the various wave-lengths. Column 8 gives the value of  $\beta$ , the difference between the absorption of the colloidal solution and the supporting medium, water. The last column contains the values of the refractive indices calculated from the fundamental equation.

Tables V., VI. and VII. contain the data for the platinum colloids reported in the same order as those for silver. The results in Table IV. were obtained with water as a supporting medium, and those in Tables V. and VI. with ethyl malonate as the supporting medium. The various concentrations  $\mu$  are given at the bottom of each table.

Table IV. gives the results obtained in the case of colloidal gold in ethyl malonate, and Table IX. contains the absorption coefficients of water and of ethyl malonate, for the slit width and width of the bolometer strips employed throughout the research.

Table X. contains the values of the absorption coefficients of the metals gold, platinum and silver taken from the work of Rubens<sup>1</sup> and Hagen. Values which were not given by them and which were necessary for the present work were obtained by plotting the values given by them and drawing a smooth curve through those points. The necessary values were obtained from this curve and are given in the table.

<sup>1</sup> Loc. cit.

In Table VIII. are reported the data for the turbid medium made from gum mastic. The values of the absorption coefficients t are

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given for two concentrations, one being twice the other.

To obtain curves shown as Fig. 1, the absorption coefficients were plotted as ordinates and the wave-lengths as abscissæ. The

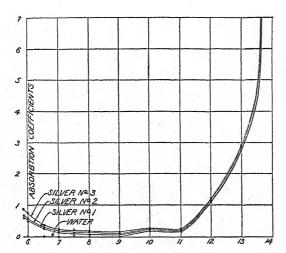


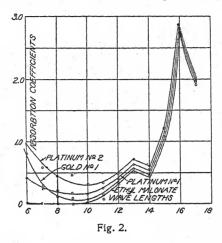
Fig. 1.

lowest of these curves represents the absorption curve of water, and the remaining three are the absorption curves of the three silver colloids used to obtain the data in Tables I., II. and III.

The uppermost of the four curves shown in Fig. 2, is the absorption curve of the gold colloid, obtained from the data of Table IV., the lowest is the curve of ethyl malonate, and the remaining two curves are those for the platinum colloids of Tables V. and VI.

In order to show graphically the manner in which the absorption due to the presence of the particles alone varied with the wavelength, the values in columns 4 and 5 for each table containing the data for the determination of the value of n, have been plotted as a function of the wave-length (Fig. 3). These curves show the ratio of the energy transmitted by the supporting medium, for a given thickness and for the various wave-lengths within the range of observation. They bring out clearly the effect of these minute particles upon the absorption of light, showing that they are less and less

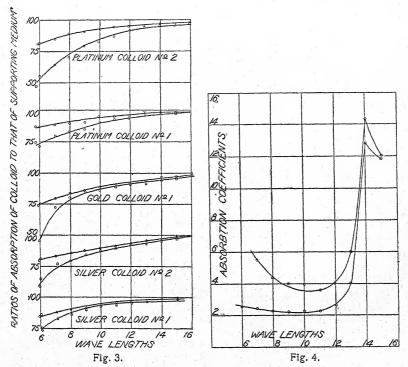
effective as we proceed to the longer wave-lengths, the absorption of the colloidal solution being almost identical with the absorption of the supporting medium. The greatest effect is somewhere in the region of the visible spectrum, in all probability where Ehren-



haft 1 and Müller 1 concluded from their results that optical resonance occurred.

In view of these results, the question at once arises concerning the numerical relationship between the values of the absorption coefficients and the wave-lengths. Lord Rayleigh in his earlier work upon the subject of atmospheres containing suspended insulating particles has shown from theoretical considerations that for such an atmosphere containing these particles, whose sizes are small compared to a wave-length, the absorption varies inversely as the inverse fourth power of the wave-length. We have sufficient data given here to investigate the relationship for colloidal If for the short range of wave-lengths just beyond the wave-length  $5.80 \times 10^{-5}$  cm. we assume that the absorption due to the supporting medium is negligible, we can see from the character of the absorption curves of the colloids that no such  $\lambda^{-4}$  relationship seems to exist between the absorption coefficients and the wave-lengths. One cannot put this investigation to too rigorous a test owing to the fact that the range for determining a relationship

of this nature is too limited. Furthermore, we cannot expect such a relationship to hold near a region of optical resonance, such as we know to exist in the case of these colloidal solutions, at a very short distance from the sodium lines of the spectrum. The data



obtained in this investigation give rise to no definite relationship between the absorption coefficient and the wave-length, with regard to colloidal solutions.

We may digress here for a moment to consider the case for which the relationship given by Lord Rayleigh, for insulating particles, should hold. In Table VIII. are given data for such a medium made of gum mastic, and the results are plotted in Fig. 4. Again assuming that the absorption of the supporting medium may be neglected where it is small, we can roughly determine the relationship between the absorption and the wave-length. A simple calculation shows that the absorption varies roughly as the inverse first power of the wave-length, which does not conform to the demands made by the

Rayleigh formula. In Table VIII. are also included the ratios of the difference between the absorption of the turbid medium and its supporting medium for the two concentrations used in obtaining the data. The ratios show that the absorption varies directly as the concentration.

TABLE I.

Silver Colloid No. 1 in Water.

Wave- length in cm.	2 / <sub>1</sub>	3 I <sub>2</sub>	$\frac{I_1^0}{I_1}$	$\frac{I_2^0}{I_2}$	$\frac{I_1}{I_2}$	7	-	8 t—w		$\frac{9}{(a^2-2v^2)^2} \frac{(a^2-2v^2)^2}{9av^2\mu}$	10
5.89×10-	86.0	66.2	86.0	66.2	1.30	.5721×	10-5	.5721×	10-5	.602	.35
6 "	87.3	74.8	86.3	73.8	1.165	.3400	"	.3400	46	1.061	.36
7 "	90.0	84.7	87.5	83.7	1.062	.1561	"	.1561	"	2.947	.46
8 "	81.3	87.3	89.5	85.4	1.046	.1220	"	.1220	"	4.215	.52
9 "	92.9	90.0	91.0	89.0	1.033	.1099	"	.0767	"	7.430	.57
10 "	92.3	85.8	92.3	92.3	1.076	.2740	"	.0595	"	10.246	.61
11 "	92.2	86.8	94.5	93.2	1.062	.2386	"	.0400	"	16.020	.64
12 "	82.3	63.9	95.8	95.5	1.287	1.1223	"	.0267	"	24.660	.66
13 "	68.2	37.4	96.0	93.5	1.823	2.8943	"	.0253	"	26.84	.68
14 "	19.4	2.42	97.5	97.0	8.010	10.786	"	.0203	"	34.45	.70
15 "	43.3	7.80	98.7	97.5	5.515	9.4831	"	.0177	"	40.70	.72

 $\mu = 2.12 \times 10^{-5}$ .

TABLE II.

Silver Colloid No. 2 in Water.

	Wa lengt cn	h in	2 I <sub>1</sub>	3 I <sub>2</sub>	$\frac{I_1^0}{I_1}$	$\frac{I_2^0}{I_2}$	$\frac{I_1}{I_2}$	7 \$		8 t—w	$\frac{9}{(a^2-2v^2)^2} \frac{(a^2-2v^2)^2}{9av^2\mu}$	10 n
	5.89	×10 <sup>-5</sup>	81.0	57.0	81.0	57.0	1.42	.8844×	(10-5	.8844×10 <sup>-5</sup>	.444	.38
	6	"	82.5	66.8	81.5	65.8	1.253	.5000	"	.5000 "	.780	.39
	7	"	86.0	79.3	83.5	78.1	1.084	.2077	"	.2077 "	2.166	.45
	8	44	87.1	81.8	85.5	79.9	1.065	.1845	"	.1710 ''	3.099	.53
	9	44	89.1	85.0	87.4	84.0	1.048	.1583	"	.1251 ''	5.463	.56
1	0	"	89.6	82.6	89.6	88.8	1.084	.2981	"	.0831 ''	7.460	.62
1	1	"	89.1	83.5	91.5	89.9	1.067	.2546	"	.0560 ''	11.780	.66
1	2	4.6	80.2	62.1	93.4	92.8	1.291	1.1326	"	.0370 ''	18.10	.67
1	3		67.3	36.8	95.0	92.0	1.830	2.903	"	.0340 ''	19.71	.67
1	4	"	19.25	2.40	97.0	96.0	8.024	10.7935	"	.0275 "	25.30	.69
1	.5	: 66	38.4	6.9	98.5	86.0	5.521	9.4891	""	.0237 "	29.90	.71

 $\mu = 2.76 \times 10^{-5}$ .

It was shown in the fundamental equation which was derived to fit the general case of colloidal solutions that the absorption due to the small metallic particles, small compared to a wave-length, was directly proportional to the concentration when the absorption of the supporting medium could be neglected. It was also shown

TABLE III.

Silver Colloid No. 3 in Water.

Wave length cm.	-	2	3 / <sub>2</sub>	$\frac{I_1^0}{I_1}$	$\frac{\frac{5}{I_2^0}}{I_2}$	6 I <sub>1</sub> I <sub>2</sub>	7 £	8 t-w	$\frac{\frac{9}{(a^2 - vv^2)^2}}{9av^3\mu}$	10 n
5.89×1	0-5 89	0.0	76.0	89.0	76.0	1.17	.5224×10	-5 .5224×1	0-5 .879	.28
6 "	90	).5	82.7	89.5	81.7	1.094	.2105 "	.2105 '	1.14	.34
7 "	94	1.1	90.6	91.5	89.6	1.038	.0963 "	.0963 '	4.30	.42
8 "	94	1.3	92.1	92.5	90.3	1.024	.09426 ''	.08126 '	6.153	.50
9 "	9	5.5	91.5	93.5	90.5	1.044	.08330 "	.0500 4	10.84	.54
10 "	94	1.3	87.9	94.3	94.3	1.072	.2550 ''	.0403 '	' 14.95	.60
11 "	92	2.6	87.1	95.0	93.6	1.062	.2358 ''	.03721 '	17.49	.65
12 "	82	2.2	63.9	95.7	95.5	1.285	1.1130 "	.0184 '	36.0	.66
13 "	68	3.8	38.6	97.0	96.5	1.783	2.7863 "	.0173	4 39.2	.68
14 "	19	9.5	2.46	98.0	97.9	7.926	10.7199 "	.0139 '	6 50.3	.70
15 "	4:	3.6	8.1	99.0	98.5	5.382	9.4777 "	.0123	59.4	.73

 $\mu = 1.45 \times 10^{-5}$ .

that in general, when the absorption of the supporting medium could not be neglected, that the difference between the absorption of the colloidal solution and the supporting medium was proportional to the concentration. If we take the ratio of (t-w) for any two concentrations for a given wave-length, the result should be equal to the ratio of the concentrations. Table XI. contains the results of such computations for the colloids of platinum and silver. At the bottom of each column is given the ratio of the concentrations. The results contained therein show conclusively that the relationship deduced from the theory is correct. The range over which these values extend is about three times the length of the visible spectrum and yet there are no evidences of marked regular deviation from proportionality. In this connection it must be borne in mind that an error of a fraction of one per cent. in the experimental determination of  $I_1$  and  $I_2$  introduces a very large error in the value of the

absorption coefficient, owing to the fact that the expression for the absorption contains a logarithmic function, and hence any regular deviation from the prediction by the analysis would make itself evident when the absorption coefficient had been determined.

TABLE IV.

Gold Colloid in Ethyl Malonate.

1en	I Vave- igth in cm.	2 I <sub>1</sub>	3 I <sub>2</sub>	$\frac{4}{I_1^0}$	$\frac{5}{I_2^0}$	$\frac{I_1}{I_2}$	7 ±		8 t—w	$\frac{9}{(a^2-2v^2)^2}$ $\frac{(a^2-2v^2)^2}{9av^3\mu}$	10
5.8	9×10⁻⁵	75.2	45.0	75.1	45.0	1.672	1.008 ×	10-5	1.008 ×10 <sup>-5</sup>	.4088	.45
6		77.81	49.31	76.2	48.3	1.578	.9626	"	.0626 "	.4988	.48
7	"	84.90	77.61	80 1	73.9	1.093	.2290	"	.2290 "	2.640	.60
8	"	90.23	86.75	84.3	80:9	1.040	.1151	"	.1153 "	6.250	.71
9	"	93.50	91.13	86.1	85.1	1.026	.0860	"	.0740 "	10.403	.77
10	"	92.87	90.69	87.2	83.0	1.024	.0850	"	.0490 "	16.67	.82
11	"	96.50	93.68	91.0	87.5	1.030	.1147	"	.0341 "	24.93	.85
12		94.72	87.30	92.0	91.9	1.085	.3642	"	.02324 ''	37.42	.87
13	"	96.10	78.64	94.2	90.2	1.222	.5624	"	.01772 ''	50.20	.89
14		96.81	88.17	94.9	97.0	1.098	.4856	"	.01280 "	64.39	.90
15	"	95.50	77.39	96.5	94.5	1.234	1.1701	"	.01126 "	80.80	.91
16	"	81.25	50.94	98.0	97.5	1.595	2.8872	"	.00928 ''	99.93	.93
17		74.90	55.40	98.6	99.0	13.57	2.8963	"	.00762 ''	123.3	.94
18	"	88.00	59.37	99.0	99.0	14.77	2.6183	"	.00652 "	146.52	.95

 $\mu = .759 \times 10^{-5}$ .

It has thus been shown that for the colloidal solutions investigated, the absorption is directly proportional to the concentration, and that furthermore, the conditions for the application of the analysis for the determination of the refractive indices of the metals is warranted; namely, that there are many particles to the wave-length. This confirms the results obtained by Mie,¹ from purely theoretical considerations, and also agrees with the direct experimental results obtained by Zsigsmondy¹ and Siedentopf, who by ultra-microscopic means found that these colloidal particles are small compared to a wave-length and are spherical in shape.

If in the application of the analysis we find that the values for the refractive indices remain constant for a given wave-length, for any metal, no matter what the supporting medium is, we are further assured of the correctness of the deductions. The values of n ob-

TABLE V.

Platinum Colloid No. 3 in Water.

Wave- length in cm.	2 I <sub>1</sub>	3 I <sub>2</sub>	$\frac{I_1^0}{I_1}$	$\frac{5}{I_2^0}$	$\frac{I_1}{I_2}$	. 7 .t	-	<i>t</i> —₁υ	$\frac{9}{(a^2-2v^2)^2}$	10
5.89×10 <sup>-5</sup>	69.20	34.77	68.2	34.7	1.990	1.500	×10 <sup>-5</sup>	1.500 ×10 <sup>-5</sup>	10.32	1.75
6 - "	73.41	35.79	72.5	34.9	2.051	1.596	"	1.596 ''	10.93	2.40
7 "	81.23	51.70	79.0	50.2	1.571	1.177	"	1.177 "	16.63	3.45
8 ""	84.10	62.15	82.5	61.0	1.353	.907	**	.907 "	22.14	4.1
. 9	85.98	69.11	84.0	68.6	1.244	.726	"	.726 "	27.56	4.3
10 "	87.07	70.90	87.0	76.2	1.228	.7918	"	.5768 ''	35.08	4.4
11 "	88.16	76.79	90.0	82.2	1.184	.6860	"	.4870 ''	42.00	4.5
12 "	78.92	56.18	91.0	84.3	1.387	1.4532	"	.3576 ''	54.77	4.62
13 "	64.75	33.81	91.2	77.0	1.915	3.1281	"	.3591 ''	55.05	4.75
14 "	18.51	21.79	93.3	87.0	8.492	11.0887	"	.3127 ''	62.32	4.82
15 ''	41.25	71.57	93.9	89.5	5.762	9.7281	"	.2627 "	71.79	4.85
16 "	51.47	12,44	95.1	92.4	4.134	8.4085	"	.2085 ''	81.39	4.89
17 "	46.42	14.86	96.0	91.1	3.122	7.1656	"	.2156 ''	88.09	4.92

 $\mu = 2.18 \times 10^{-5}$ .

TABLE VI.

Platinum Colloid No. 2 in Ethyl Malonate.

Veng	i ave- th in m.	2 / <sub>1</sub>	3 I <sub>2</sub>	$\frac{I_1^0}{I_1}$	$\frac{5}{I_2^0}$	$\frac{I_1}{I_2}$	7 *		8 t—w		$\frac{9}{(a^2-2v^2)^2}$	10 n
5.89	×10 <sup>-5</sup>	80.21	48.00	78.9	47.5	1.671	.6458×	(10-5	.6458×	10-5	10.32	1.40
6	-66	81.40	56.53	80.5	56.0	1.440	.8114	"	.8114	"	10.93	2.55
7		85.64	65.71	87.2	64.0	1.288	.5918	"	.5918	66	16.63	3.59
8		89.30	76.65	82,7	71.5	1.165	.4549	"	.4549	44	22.14	4.05
9	"	93.31	81.01	86.5	75.9	1.153	.4753	"	.3633	44	27.56	4.30
10	66	95.52	87.55	90.0	83.3	1.091	.3261	"	.2911	"	35.08	4.49
11	"	97.81	91.84	93.0	87.1	1.065	.2540	"	.2454	66	42.00	4.59
12		96.80	86.57	94.0	91.2	1.117	.4939	"	.1799	"	54.77	4.67
13	- 44	96.02	82.61	94.1	93.0	1.163	.7252	"	.1805	"	55.05	4.81
14	"	96.91	86.29	95.0	94.5	1.123	.6299	"	.1571	"	62.32	4.86
15	44	94.60	76.85	95.5	93.2	1.231	1.1901	***	.1326	"	71.79	4.89
16	"	79.59	49.01	96.0	93.3	1.624	2.8732	"	.1148	"	81.39	4.93
17	"	73.32	53.40	96.7	95.5	1.373	1.9947	"	.1060	**	88.09	5.15

 $\mu = 1.091 \times 10^{-5}$ .

tained for gold, platinum and silver show that they are independent of the supporting medium. The values of the refractive indices for silver range from 0.34 for the wave-length  $5.89 \times 10^{-5}$  to 0.72 for the wave-length  $15 \times 10^{-5}$  cm. The values for platinum begin with 1.48 at the wave-length  $5.89 \times 10^{-5}$  cm. and rise steadily to 5.02 at a wave-length  $17 \times 10^{-5}$  cm., while for gold the values extend from 0.45 to 0.95 for the wave-lengths,  $5.89 \times 10^{-5}$  cm. to  $18 \times 10^{-5}$  cm. respectively.

TABLE VII.

Platinum Colloid No. 1 in Ethyl Malonate.

len	I Vave- gth in	2 I <sub>1</sub>	3	$\frac{I_1^0}{I_1}$	$\frac{5}{I_2^0}$	$\frac{I_1}{I_2}$	7	-	±—10		$\frac{9}{(a^2-2v^2)^2}$	10 n
5.89	9×10-5	87.0	74.89	87.0	74.9	1.163	.3282×	10-5	.3282×	10-5	10.32	1.30
6	"	88.4	72.40	87.5	71.5	1.221	.4262	66	.4262	"	10.93	2,40
7	66	95.2	84.86	89.0	80.8	1.123	.3129	"	.3129	"	16.63	3.50
8	"	96.03	88.50	89.9	82.8	1.085	.2429	"	.2429	66	22.14	4.0
9	66	97.5	91.89	90.5	85.7	1.061	.1985	"	.1835	"	27.56	4.2
10	4.6	98.49	94.43	93.1	40.0	1.043	.1563	"	.1527	"	35,08	4.5
11	"	99.83	96.64	94.2	92.7	1.033	.1401	"	.1315	"	42.00	4.6
12	66	97.61	89.00	94.8	93.7	1.096	.4100	"	.0960	"	54.77	4.65
13		97.10	85.03	95.2	97.5	1.142	.6412	"	.0965	"	55.05	4.80
14	"	97.89	87.95	96.0	96.5	1.113	.5556	"	.0828	"	62.32	4.85
15	"	95.81	78.09	96.8	95.1	1.227	1.7277		.0702	"	71.97	4.90
16		80.59	51.43	97.1	98.0	1.567	2.8186	"	.0602	"	81.39	4.95
17	"	74.40	54.58	98.0	97.5	1.363	1.9475		.0588	"	88.09	.05

 $\mu = .584 \times 10^{-5}$ .

It was quite surprising to learn that the values of the refractive indices increased with increasing wave-length, yet after having found this to be the case, it was at once apparent that the behavior of the metals as regards their reflection would lead one to expect that there should be found a region of anomalous dispersion, extending into the infra-red, and having its origin in the region of the visible spectrum.

Drude 1 and Kundt 2 have obtained values of the refractive indices for the metals, gold, platinum and silver, at a wave length  $5.89 \times 10^{-5}$  cm., the values for the above metals are 0.38, 2.1 and

<sup>&</sup>lt;sup>1</sup>Theory of Optics, p. 366.

<sup>&</sup>lt;sup>2</sup> Phil. Mag., 26, p. 5.

o.18 respectively. The values obtained in this paper do not agree very closely with those obtained by these observers. The values reported by Drude were obtained by a katoptric method, which is open to the objection that it is indirect and that large experimental error may be introduced both in observation and by the existence of surface films on the metallic surfaces.

TABLE VIII.

Absorption Coefficients.

	1 ×		0	f Gum I	lastic N	o. 1.	*	
Wave- length in cm.	$I_1$	$I_2$	$\frac{I_1^0}{I_1}$	$=\frac{I_2^0}{I_2}$	$\frac{I_1}{I_2}$	t'	t'w	
5.89×10 <sup>5</sup>								
6 " 7 "	38.0	4.9	7.75	4.85	7.75	5.51 ×10 <sup>-5</sup>	5.51 ×10-5	
8 "	47.5	10.5	46.5	10.3	4.50	4.448 "	4.448 ''	
9 "	57.0	16.5	56.0	16.2	3.45	4.118 "	4.118 ''	
.0 "	65.0	22	65.0	23.5	2.95	4.000 "	3.78 "	
1 "	68.0	28	70.0	30.2	2.43	3.619 "	3.42 "	
2 "	65.0	26	76.0	39.0	2.50	4.080 "	3.00 "	
3 "	56.0	16	79.0	40.0	3.50	6.032 ''	4.27 "	
4 "	29.5	2.0	67.8	79.0	14.74	13.96 "	3.20 "	-
15 "	39.1	5.7	89.0	71.0	6.8	10.65 "	1.19 "	

Of Gum Mastic No. 2.

leng	ave- gth in m.	$I_1$	$I_2$	$\frac{I_1^0}{I_1}$	$\frac{I_2^0}{I_2}$	$\frac{I_1}{I_2}$	ŧ	t-w	$\frac{t'-\tau}{t-w}$
5.89	9×10-5	-				-			
6	"	62.0	19.1	3.26	61.5	18.8	2.522×10 <sup>-5</sup>	2.522×10-5	
7		68.5	25.9	2.64	66.5	25.7	2.513 "	2.513 "	2.2
8		75.0	34.0	2.21	73.5	33.2	2.344 "	2.344 "	1.9
9	46	80.0	41.0	1.95	78.0	40.5	2.223 "	2.223 "	1.86
10		86.0	47.1	1.83	86.0	50.5	2.230 "	2.00 "	1.68
11		88.0	52.3	1.69	90.5	56.0	2.134 "	1.94 ''	1.70
12	**	78.1	43.0	1.82	91.0	64.1	2.664 "	1.57 "	1.54
13	"	65.0	28.0	2.32	91.5	70.0	4.043 "	2.28 "	1.94
14	"	21.1	1.9	11.1	93.2	76.0	12.474 "	1.70 "	1.90
15	"	40.9	68.2	5.77	93.0	85.0	10.06 "	6.0 "	2.0

Kundt's method was a very direct one. He succeeded in obtaining very acute-angled prisms, to which he applied the ordinary

method for determining the value of n. This method is open to the objection that it is highly probable that such metallic prisms are not homogeneous in structure, and it is a very difficult task to obtain a measurement, by means of such small angled prisms.

The method of this paper is a direct one from an experimental point of view, and the measurements are capable of considerable accuracy, if carefully taken and with accurate apparatus. The fundamental assumptions make the method of finding an equation for n an indirect one, but it is no more indirect than Drude's method of obtaining n, in terms of the azimuth of restored polarization and the principal angle of incidence.

TABLE IX.

Absorption Coefficients.

٠,	Wave-		Ethy	i Malo	nate.		337	ave-		v	Vater.		
	ngth in cm.	<i>I</i> <sub>1</sub> °	$I_2{}^0$	$\frac{I_1^0}{I_2^0}$	ขบ		len	gth in	$I_{1}^{0}$	$I_2^{\ 0}$	$\frac{I_1^0}{I_2^0}$	ขข	
5.8	89×10 <sup>-5</sup>	100	100	1.00	. 0		5.8	9×10-5	101	101	1.00	0	
6	"	101	101	1.00	0		6	**	101	101	1.00	0	
7		105	105	1.00	0		7	**	103	103	1.00	0	
8	"	107	107	1.00	. 0		8	66	102	102	1.00	0	
9	44.	108.5	107	1.01	.0120×10	)-5	9	- "	102	101	1.01	.0033>	<10 <sup>-4</sup>
10	"	106.1	105.2	1.01	.036 "		10	"	100	93.0	1.06	.2150	"
11	"	106.0	104.0	1.02	.0806 "		11	66	97.5	93.0	1.05	.1986	"
12	**	103.0	95.0	1.08	.3140 ''		12		86.0	67.1	1.28	1.0956	"
13	"	102.0	87.0	1.12	.5447 "	1	13	"	71.1	40	1.78	2.769	"
14	6.6	102.0	91.0	1.094	.4728 ''		14	"	19.95	2.5	7.98	10.766	44
15	"	99.1	82.1	1.21	1.0575 "		15	"	44.0	8.0	5.50	9.465	"
16	"	83.0	52.5	1.592	2.7584 "		16		54.0	13.5	4.0	8.700	"
17	"	76.1	56.0	1.35	1.8887 "		17	66	49.0	16.27	3.013	6.950	
18	. 46	89.0	60.0	1.48	2.6118 "	-	18	"			200		

The final and most striking test of the correctness of the values of n obtained by the method of this paper is by means of an equation deduced by Drude<sup>1</sup> for the reflection coefficient in terms of the absorption coefficients a, and the refractive indices n. The equation is

$$R = \frac{(n^2 - 1)^2 + a^2}{(n^2 + 1)^2 + a^2}.$$

<sup>&</sup>lt;sup>1</sup> Physik des Aethers, p. 457.

The values of the absorption coefficients are known from the work of Rubens 1 and Hagen, and the same investigators have obtained accurate measurements of the reflection coefficients. Substituting the values of n given in this paper and the values of  $\alpha$ , the values of R, thus computed, should agree with the observed values of R. Table XII. contains the results of such computations. computed and observed values of R show a remarkable agreement in the case of silver, and the agreement in the case of platinum and gold is very good. It will be noticed that an error in n, would, on account of the fact that it enters as the second power in the above equation, produce a correspondingly greater error in the calculated value of the reflecting power of the solid metal. In view of the good agreement between calculated and observed values of R, it seems that the correctness of the values of n reported in this paper is placed beyond question.

TABLE X. Absorption Coefficients.1

Wave-lengt	n Plat	inum.	G	old.	Si	lver.
in cm.	а	$a^2$	а	$a^2$	a	a <sup>2</sup>
5.89×10-	4.08	16.65	2.82	7.95	3.67	13.47
6 "	4.16	17.30	2.91	8.49	4.20	17.64
7 "	4.81	23,13	4.13	17.06	5.52	30.47
8 "	5.36	28.83	5.19	26.94	6.21	37.70
9 "	5.94	34.28	6.00	36.00	7.25	52.56
10 "	6.47	41.86	6.90	47.61	8.00	64.00
11 "	6.85	46.92	7.80	60.84	9.15	83.40
12 "	7.85	61,65	8.85	78.33	10.3	110.0
13 "	7.87	61.93	9.70	94.04	10.9	118.8
14 "	8.32	69.22	10.5	110.25	11.8	138.2
15 "	8.93	79.27	11.3	127.69	12.4	153.96
16 "	9.38	88.34	12.1	146.41	2 1	
17 "	9.80	95.04	13.0	169.10		100
18 "		1.0	13.7	187.67	3	

#### Conclusion.

In the endeavor to supplement the existing data obtained for colloidal solutions and turbid media in the visible spectrum by extending the field of investigation into the infra-red region of the spectrum

<sup>&</sup>lt;sup>1</sup> Phil. Mag., 7, p. 157, 1904.

TABLE XI.

Silver.

Platinum.

Wave- length in	(t-w) for No. 1	(t-w) for No. 1	(t-w) for No. 2	(t-w) for No. 1	(t-70) for No. 1	(t-w) for No. 2
cm.	(t-w) for No. 2	(t-w) for No. 3	(t-w) for No. 3	(t-w) for No. 2	(t-w) for No. 3	(t-w) for No. 3
5.89 10-5	.65	1.10	1.69	.50	.21	.427
6 "	.68	1.62	2.40	.517	.265	.51
7 "	.75	1.66	2.04	.517	.265	.50
8 "	.70	1.50	2.01	.53	.26	.52
9	.61	1.52	2.50	.50	.25	.50
10 "	.71	1.49	2.07	.52	.26	.50
11 "	.715	1.08	1.51	.54	.27	.50
12 "	.73	1.45	2.05	.50	.265	.49
13 "	.735	1.46	2.01	.50	.27	.50
14 "	.736	1.46	2.01	.51	.257	.49
15 "	.747	1.44	2.02	.54	.27	.50
16 "				.52	.28	.53
17 "		1	,	.55	.24	.38
Mean	.706	1.43	2.03	.52	.26	.50
Ratios of Concentra- tions.	$\frac{\text{No. 1}}{\text{No. 2}} = .76$	$\frac{\text{No. } 1}{\text{No. } 3} = 1.46$	$\frac{\text{No. } 2}{\text{No. } 3} = 1.94$	$\frac{\text{No. } 1}{\text{No. } 2} = .537$	$\frac{\text{No. 1}}{\text{No. 3}} = .27$	$\frac{\text{No. 2}}{\text{No. 3}} = .50$

as far as present means will permit, the writer, by the help of the analysis developed in the course of the research, has arrived at the following conclusions:

- 1. That the difference between the absorption of the colloidal solution and the absorption of the supporting medium is directly proportional to the concentration. For turbid media this cannot be said to be the case, generally, owing to the variation of the size of the particles for different media.
  - 2. That the Rayleigh formula,

$$H=\frac{32\pi(n^2-1)}{3n\lambda^4},$$

where H is the absorption, n the refractive index of the particle, and  $\lambda$  the wave-length, holds neither for the case of turbid media, for which it was developed, nor for colloidal solutions. The law of absorption cannot be stated definitely from this work.

3. That the values of the refractive indices n, for the metals, determined by this method are independent of the supporting medium and are strictly inherent in properties of the metals themselves.

TABLE XII
Refractive Indices.

	Rubens and Hagen.		84.4	91.8	94.9	96.4	94.7		97.6			97.3			
Gold.	R Computed,	82.4	82.8	9.78	90.5	92.2	91.8	94.6	95.8	96.4	0.76	97.6	97.4	6.76	98.4
	Colloid.	.45	.48	9.	.71	.77	.82	.85	.87	68.	96.	.91	.93	.94	95
	Rubens and Hagen.	91.6	97.6	94.6	96.3	0.96	6.96	*	97.1			98.4	4		
	R Computed.	91	92.7	94.7	95.0	96.0	96.3	97.2	9.76	0.86	98.3	98.4		*	
Silver.	Mean.	.34	.36	.44	.52	.56	19.	.65	99.	89:	.70	.72			
	Colloid No. 3.	.28	.36	.42	.50	.54	09.	.65	99.	.68	.70	.73			
	Colloid Colloid Colloid No. 2. No. 1. No. 3.	.35	.36	.46	.52	.57	.61	.64	99.	89:	.70	.72			
	Coffoid No. 2.	.38	.39	.45	.53	.56	.62	99:	.67	19.	69.	.71			
	Rubens and Hagen.		64.2	69	70.3	73.6	75.5		77.7			79.0			
	R. Computed.		66.5	67.8	70.2	73.1	75.2	76.4	79.8	80.0	81.3	83.0	84.0	85.0	
-	Меап	1.48	2.44	3.51	4.05	4.27	4.47	4.57	4.65	4.79	4.84	4.88	4.92	5.03	
Platinum.	Colloid No. 3.	1.75	2.40	3.45	4.10	4.30	4.40	4.50	4.62	4.75	4.82	4.85	4.89	4.92	
д	Colloid No. 2.	1.40	2.55	3.59	4.05	4.30	4.49	4.59	4.67	4.81	4.86	4.89	4.93	5.15	
	Colloid No. r.	1.30	2.40	3.50	4.00	4.20	4.50	4.60	4.65	4.80	4.85	4.90	4.95	2.00	
	Wave- length in cm.	5.89×10-6	" 9	,, 1	8	., 6	10 "	", 11	12 - "	13 "	14 "	15	., 91	17	., 81

4. That the final test as to the correctness of the analysis, by means of the equation of Drude,

$$R = \frac{(n^2 - 1)^2 + a^2}{(n^2 + 1)^2 + a^2},$$

where R is the reflection coefficient and a the absorption coefficient, places the values of the refractive indices obtained for the metals gold, silver and platinum beyond question.

The writer wishes to express his gratitude to Professor A. Trowbridge at whose suggestion and under whose direction and advice, the work was finally brought to its present state. The writer also expresses his indebtedness to Professor G. A. Hulett for valuable suggestions and aid in the construction of the standard batteries.

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# ON THE BURSTING STRENGTH OF GLASS TUBING.

By J. R. ROEBUCK.

THE bursting strength of a number of samples of glass tubing were determined as a preliminary to some work with high pressures in glass apparatus. Similar work has already been published by Bradley and Browne 1 but they worked only over narrow ranges of bore and wall. In view of the small amount of data on this subject, it seemed profitable to extend this preliminary series and to publish the results.

The glass was ordered from Eimer and Amend, German soda glass specified, and the maker's name requested. After the work was under way it was ascertained that the tubing had been picked from the stock on their shelves and possibly came from more than one maker. Some of the variation in the results may be due to this cause but the work of Winklemann and Schott has shown a variation in the tensile strength of only about a factor of three with extreme variation in the composition. Generally the samples handled similarly in the blowpipe and joined readily to the capillary tubing employed as leads. This tubing of soft German soda glass is the kind generally used in glass apparatus and consequently the kind a knowledge of whose strength is the most useful.

For the sake of uniformity the shape of tube employed in the preliminary tests was used throughout practically the whole series. In the case of a few of the heavy walled tubes however it was necessary to mount them directly in the machine as the leads often fell below them in strength. The tubes to be tested were drawn down at both ends to 1 mm. or less bore and about 3 mm. wall and one capillary end sealed. The part of the tube free of constriction was 15 cm. or more except in a very few instances where the chances of glass working in heavy walled tubing made them a few cm. less.

<sup>&</sup>lt;sup>1</sup> Jour. of Phys. Chem., 8, 37, 1904.

A number of samples of different glasses were tried first and they all showed the presence of heavy strain by their repeated cracking in the flame. This conclusion was checked by immersing the tubing in a mixture of aniline and alcohol of approximately the same refractive index as the glass, to exclude lens effects, and examining between crossed nicols. It was immediately apparent that the glass would all require careful annealing both before and after working in the flame. The preliminary annealing was necessary as otherwise the tubing flew to pieces repeatedly during the most cautious heating in the smoky flame. Accordingly an electric furnace consisting of a porcelain tube wound with nickel wire, was built and well covered with asbestos packing. An iron-copper thermo-couple with one junction exposed to room temperature served to duplicate the temperature employed which was fixed by observing the galvanometer deflection when a long rod through the furnace could be slightly but permanenly bent. The E.M.F. had fallen almost to zero again and corresponded to a temperature in the neighborhood of 500° C. The procedure was to heat the furnace filled with tubes slowly to this temperature, requiring close to an hour, hold at this temperature for about an hour and allow to cool spontaneously, usually over night. Under this treatment the glass tubes never stuck together nor to the furnace but required careful support throughout their length. The tubes so treated showed absolutely no illumination between crossed nicols.

The difficulty of joining glass and metal tubing has been a source of constant annoyance to those attempting it. In some of his papers Kammerling Onnes¹ refers to "Cailletet's method" but gives a very meager description of the method he uses. It seems to be substantially as follows. The glass tube, swelled or constricted slightly in one or two places, is first coated with a film of platinum or silver. The silver may be put on in an ordinary silvering bath but is more trouble than the plantinizing. A good conducting film of platinum² may be obtained by brushing over the glass a water solution of platinum chloride and dextrine, say one or two per cent. of each, drying the tube well above the flame of a Bunsen burner and

<sup>&</sup>lt;sup>1</sup>Proc. Amsterdam Acad., 8, 75, 1905.

<sup>&</sup>lt;sup>2</sup> Threlfal, Laboratory Arts.

finally incinerating directly in the flame. Any small flakes of platinum may be brushed off with a soft wad of cotton and the film will be bright, conducting but semi-transparent. This is then copper plated from .5 to I mm. thick and 3 to 4 cm. along the tube. a loop of wire around the tube serving for preliminary contact. Sweating into a brass or iron tube finishes the joint. One of these joints has been in satisfactory use in a vacuum apparatus in this laboratory for months. I have had several carry 670 atmospheres pressure without leak or rupture. The glass rarely breaks inside the metal and will stand rough treatment, for example, cooling the metal of the sweated joint with wet cotton, which was the regular proceeding with the 6 mm. capillary tubing joints. The metal clings to the glass strongly as shown by it requiring 300 atmospheres on the end of a 6 mm. capillary tube to make the glass slip inside the metal sheath although the glass was a plain cylinder without constriction or enlargement. Small bubbles in the thin copper sheath were frequently noticed, apparently due to the vapor pressure of water included during the plating, and these bubbles always left the glass at a considerable angle. It is difficult to speak highly enough of the exceedingly satisfactory performance of these joints.

In making the tests the annealed tubes were joined to previously prepared glass capillary leads and this joint annealed only in the smoky flame. The capillary was sweated to the connector for the Cailletet pump and the pressure applied steadily with the pump for low pressures and in increments of about 5 atmospheres for the high pressures using the screw plunger, until the tube burst. In cases where the capillary lead burst it was replaced and the test repeated. In a few instances when the glass had been brought to near the breaking point, on repeating the application of the pressure, the tube would break much below the previous pressure. No trace of strain as indicated by double refraction could be observed in tubes either broken or unbroken by the first tests and the same phenomenon occurred after annealing between tests. It is possible that the extremely sudden shock of the first break had weakened or broken the surface under strain. Phillips 1 has shown that glass

<sup>&</sup>lt;sup>1</sup> Phil. Mag. (6), 9, 520, 1905.

rods of small cross-section steadily increase in length when subjected to tensions near the breaking tensions. The effect of such a yielding under tension in the case of tubes should be to distribute the strain deeper into the glass wall and so increase the bursting pressure. In the present case the pressure was not applied for more than a few minutes so that this effect probably had not time to show itself. It is well known that metals increase in strength when carried slightly beyond the elastic limit. These observed cases might be taken to indicate that glass tubing weakens under strain, an effect which other observers also suspect. The experiments of Phillips cited above, the results recorded by Hovestadt 1 on the tensile strength of glass bars, and the behavior of metals all point the other way. As far as these results are concerned the shock may have been the cause of weakening.

The character of the break as indicated by the fragments show that the tubes almost invariably split longitudinally, in many cases into long narrow ribbons. The capillary tubes occasionally simply split into two pieces. In case the destruction was not complete in the larger tubes, the upper end seemed more liable to complete destruction probably from the small amount of compressed air there, as no care was taken to fill the tubes completely with the oil.

A set involving 4 tests each of tubes of 1, 2, 3, 4, 5, 6, 7 mm. bore each with 1, 2, 3, 4 mm. wall was carried out as far as possible. The results of the tests are given in Table I. The measurements of the tubes were made by cutting them from the long sticks and measuring each end with a micrometer microscope. Obviously very careful measurements were not required and only tenth millimeters are recorded. The tubes varied slightly both on different diameters and at different ends, and in view of the variation in the breaking pressure, an average of these measurements seemed sufficient. In the table the bore and wall are each given in millimeters, r is the ratio  $(r_2/r_1)$  of the external to the internal radius, P is the bursting pressure in atmospheres, and T the circular tension in atmospheres on the inner surface to be described more in detail later. The list is divided into groups of roughly the same bore with increasing wall. Sets of roughly the same bore and wall, indicated

<sup>1</sup> Hovestadt, Jena Glass, Macmillan, 1902.

TABLE I.

No.	Bore.	Wall.	r	P	Av. P	T	Av.
1	1.1	1.9	2.15	>667)		1150	
2	1.1	1.9	2.15	607		1030	
3	1.1	1.9	2.15	620	570	1040	990
4	1.1	1.9	2.15	387		670	
5	1.4	3.1	5.43	640)		832	
6	1.4	3.1	5.42	>640 >	555	832	722
7	1.4	3.1	5.42	387		503	
8	1.8	1.0	2.17	300 )		518	
9	1.8	1.0	2.17	433	27.7	750	670
10	1.8	1.0	2.17	260	311	450	670
11	1.8	1.0	2.17	253		438	
12	1.9	2.9	4.05	293 )		400	
13	1.9	2.9	4.05	487		660	
14	1.9	2.9	4.05	>647	423	880	575
15	1.9	2.9	4.05	267		363	
16	2.0	4.0	5.00	527 )	× .	695	
17	2.0	4.0	5.00	400		528	
18	2.0	4.0	5.00	453	453	600	528
19	2.0	4.0	5.00	433		572	
20	3.2	0.9	1.57	315 )		770	
21	3.2	0.9	1.57	275	251	674	600
22	3.2	0.9	1.57	195	254	477	620
23	3.2	0.9	1.57	230	-	564	
24	3.3	1.4	1.82	333 )		630	
25	3.3	1.4	1.82	313 >	315	594	600
26	3.3	1.4	1.82	300		570	
27	2.8	1.7	2.14	253		490	
28	2.8	1.7	2.14	447		778	
29	2.8	1.7	2.14	413	341	720	620
30	2.8	1.7	2.14	253		490	
31	2.8	3.2	3.25	473		676	
32	2.8	3.2	3.25	520 >	431	743	615
33	2.8	3.2	3.25	300		428	
34	2.8	3.4	3.43	553 )		780	
35	2.8	3.4	3.43	367	422	513	
36	2.8	3.4	3.43	413	475	580	665
37	2.8	3.4	3.43	567	*	792	
38	3.6	1.1	1.77	280 )		630	
39	3.6	1.1	1.77	200 }	230	450	518
40	3.6	1.1	1.77	210 ]	*	472	
41	3.8	3.0	2.58	400 ]	x 2	630	
42	3.8	3.0	2.58	367	2.0	576	- 22
43	3.8	3.0	2.58	327	-	512	
44	3.9	3.0	2.54	380 }	404	596	635
45	3.9	3.0	2.54	>473		740	-
46	4.0	3.0	2.54	367		575	
47	4.0	3.0	2.54	513		804	

TABLE I.—Continued.

No.	Bore.	Wall.	r	P	Av. P	T	Av. T
48	4.4	4.0	2.82	295 )		442	
49	4.4	4.0	2.82	380 >	401	570	601
50	4.4	4.0	2.82	527		790	
51	5.5	1.0	1.36	247 ]		825	
52	5.5	1.0	1.36	230		770	
53	5.5	1.0	1.36	255	220	855	738
54	5.5	1.0	1.36	150		520	
55	5.0	2.0	1.80	333		727	
56	5.0	2.0	1.80	320		704	#10
57	5.0	2.0	1.80	380	327	837	718
58	5.0	2.0	1.80	277		610	100
59	5.0	4.0	2.60	353 7		555	
60	5.0	4.0	2.60	340 >	369	535	580
61	5.0	4.0	2.60	413		647	
62	4.8	4.0	2.46	200		320	0.00
63	4.8	4.0	2.46	245 >	247	392	394
64	4.8	4.0	2.46	295		472	
65	6.0	0.9	1.30	135 )		511	
66	6.0	0.9	1.30	180	7.77	683	572
67	6.0	0.9	1.30	120	151	455	3/4
68	6.0	0.9	1.30	170		544	
69	6.3	1.6	1.51	245)	025	640	674
70	6.3	1.6	1.51	225	235	587	614
71	6.2	3.6	2.17	290	- ,-	510	1 7
72	6.2	3.6	2.17	>600		1280	
73	6.2	3.6	2.17	280 >	350	493	616
74	6.2	3.6	2.17	300		528	1.00
75	6.2	3.6	2.17	280		493	
76	6.2	4.0	2.28	295)	0.50	514	127
77	6.2	4.0	2.28	205 }	250	356	435
78	6.6	1.2	1.36	190 )		634	-
79	6.6	1.2	1.36	170	194	567	646
80	6.6	1.2	1.36	220	194	733	040
81	6.6	1.2	1.36	195		650	1
82	6.5	1.5	1.46	160 }	215	427	573
83	6.5	1.5	1.46	270	213	720	5/3
84	6.7	3.2	1.81	212		382	
85	6.7	3.2	1.81	255 }	231	460	415
86	6.7	3.2	1.81	227		408	
87	7.0	3.5	2.00	280		512	

Average 619

by the brackets, are grouped and the averages of P and T given in the remaining columns. In a few cases the tubes were not broken and this is indicated in the table by the sign > before the value of P.

TABLE II.

Bore, mm.	Wall, 1 mm.	Wall, 2 mm.	Wall, 3 mm.	Wall, 4 mm.
1		570	555	
2	311		423	453
3	280	341	456	
4	230		404	401
5	220	327	- 1	305
6	151	235		321
7	194	215	231	280

The numbers recorded are the "Av. P" from Table I.

In Table II. are grouped diagrammatically the values of Av. P from Table I. It will be immediately obvious that the strength is not at all proportional to the thickness of wall but that added thickness produces less and less proportional effect as the wall grows thicker. It will be observed also that the bursting pressure is not inversely proportional to the bore but that the strength falls off much less rapidly than would be expected. This is to be referred to the more regular distribution of the strain in the wall with lessening curvature. In Table III. are the numbers of Table II. multiplied by the bore in millimeters and divided by the wall in millimeters and the regular variation of the numbers both horizontally and vertically emphasizes the variation from this simple relation.

TABLE III.

Bore, mm.	Wall, 1 mm.	Wall, 2 mm.	Wall, 3 mm.	Wall, 4 mm.	
1		285	185		
2	622		282	226	
3	840	512	456		
4	920		539	401	
5	1,100	817	~	381	
6	906	705		481	
7	1,358	752	539	490	

The numbers recorded are the "Av. P" of Table I. multiplied by the bore in mm. and divided by the wall in mm.

Formulæ for the strength of thick-walled tubing have been worked out in connection with problems in the design of cannon. The most

complete of these are probably Clavarino's. His formula for the distribution of circular tension in the wall of a long tube, whose ends also support the pressure, is

$$T = (I - 2e) \frac{r_1^2 p_1 - r_2^2 p_2}{r_2^2 - r_1^2} + (I + e) \frac{r_1^2 r_2^2}{r_2^2 - r_1^2} \cdot \frac{p_1 - p_2}{x^2}$$
(I)

where  $r_2$  is the external and  $r_1$  the internal radius,  $p_1$  is the internal and  $p_2$  the external pressure, x is the distance of the point being considered from the axis of the tube, and e is the coefficient of lateral contraction which is here 0.260 or one fourth. In all the cases considered in this paper  $p_2$  is not greater than one per cent. of  $p_1$ , and may be neglected. For the tension on the inner surface put  $x = r_1$  and the expression reduces to

$$T = \frac{(2+5r^2)}{4(r^2-1)}p_1 = \varphi p_1 \tag{2}$$

where  $r_2/r_1 = r$ .

For tension on the outer surface put  $x = r_2$  and

$$T_1 = \frac{1.75}{(r^2 - 1)} p_1 = \psi p_1. \tag{3}$$

In the deduction of these formulæ it has been assumed that strain is always proportional to stress, which only holds within the elastic limit. It is an open question whether glass will be permanently deformed in a short time by strains insufficient to cause fracture. For this reason and for want of any knowledge of stress and strain beyond the elastic limit equation (2) above has been applied to the calculation of the circular tension in the inner surface of the tube at the bursting pressure. The results are listed in the column T in Table I. Table IV. is similar in form to Tables II.

TABLE IV.

Bore, mm.	Wall, 1 mm.	Wall, 2 mm.	Wall, 3 mm.	Wall, 4 mm.
1		990	722	
2	670		575	528
3	620	620	615	
4	518	*	635	601
5	738	718		580
6	572	614	1, 10	616
7	646	573	415	512

The numbers recorded are the "Av. T" from Table I.

and III. and the numbers are those under Av. T from Table I., and they show no systematic variation with the variation of either bore or wall. In view of the variation of the readings for different tubes from the same stick, the values of T may be considered constant within the limits of individual observations and the rupturing surface tension set at the general average 619. It may also be concluded that this formula is satisfactory for calculation of bursting strength from this value of T within the limits of the above experiments.

The numbers given in the column headed T in Table I. are tension expressed in atmospheres. In the more usual units the general average 619 gives 6.39 kg./mm.<sup>2</sup> as the rupturing surface tension. The tables in Bradley and Browne's article cited above have been recalculated by this formula and the average value of T for each table is given in Table V. Hovestadt gives the results of Winkle-

TABLE V.

Table.	Av. T. Eqn. 2.	Av. T. Kg./mm. <sup>2</sup>	Table.	Av. T. Eqn. 2.	Av. T. Kg./mm. <sup>2</sup>
$\boldsymbol{A}$	358	3.70	D	674	6.97
$\mathcal{B}$	632	6.53	E	714	7.38
C	582	6.02	F	487	5.03

mann and Schott's tests on the tensile strength of different Jena glasses and their values, while very concordant for each glass, run from 2.8 to 9.2 kg./mm.<sup>2</sup> Kowalski <sup>1</sup> gets results from 8.5 to 8.9 kg./mm.<sup>2</sup> for the particular glass he used. The agreement between these two ways of determining the tensile strength is precisely such as the variation in composition would lead one to expect. In view of this agreement there is sufficient justification for pointing out some of the obvious results of the above formula.

As an aid in the calculation of T, the values of  $\varphi$  and r were plotted and form the upper curve in Table VI. In order to make the curve useful for small values of (r-1) the nearly vertical part of the curve has been plotted again with the scale of r multiplied by 10, and forms the curve on the right. The general curve approaches a rectangular hyperbola with asymptotes (r-1) and  $(\varphi-1)$ .

The deductions which can be made from the form of this curve will be made more evident by the lower curve which is the plot of <sup>1</sup> Wied. Ann., 36, 306, 1889.

TABLE VI.

	Curve	φ.			-		Cur	ve ψ.		
r			φ			r			ψ	
1.1			9.6			1.1			8.33	
1.12			8.13			1.11			7.53	
1.15	1		6.72			1.12			6.88	
1.2			5.23			1.15			5.43	
1.3	1		3.79	-		1.2			4.0	
1.4			3.07			1.3			2.54	
1.5	. 1		2.66			1.4			1.82	
1.6			2.37			1.5			1.40	
1.8	1		2.03			1.6			1.12	
2.0	- [		1.83			1.7			0.926	
2.2			1.70			2.0			0.583	
2.5			1.59			2.5			0.333	
3.0			1.47			3.0			0.219	
3.5			1.40			4.0			0.117	
4.0			1.37			5.0			0.070	
5.0			1.32			6.0			0.050	
6.0			1.30			7.0			0.0365	
7.0			1.28			8.0			0.0278	
8.0			1.28			9.0			0.0219	
9.0	-		1.27					-		

r and  $\psi$  where  $\psi$  is the factor for the tension in the outer surface. The curve is again approximatly a rectangular hyperbola but with the asymptotes  $(\psi - 1)$  and r. Also it approaches the axis of r much more rapidly than does the  $\varphi$  curve.

For values of r greater than about 4,  $\varphi$  becomes practically a constant and

$$T = 1.3 P$$

or the bursting pressure is independent of r, that is, independent of both internal and external radii. This is confirmed by the value of  $\phi$  at r=4, which is about 15 per cent. of  $\varphi$ , so that the outer layers of the wall with increasing values of r carry practically no tension. This had been previously observed experimentally in the behavior of capillary tubes whose walls were two to three mm. and whose bore varied from one mm. to markedly less. The rupture occurred as often in the fine part as in the larger part. It will be obvious that there is no gain in reducing the bore of an ordinary capillary tube below 1 mm.

When r becomes nearly unity, variations in r will produce variations in  $\varphi$  almost entirely in the factor (r-1). So that here

$$T = k \frac{r_1}{v} P$$

where  $w=r_2-r_1$ , which is the simple formula usually employed for thin-walled tubes. The values of r for which this formula is suitable are important. For this simple expression to hold the tension must be practically uniformly distributed through the wall. Reference to the two curves, Table VI., will show that even in the case of r=1.1 the tensions differ by 15 per cent. This is such a case as a wall of 1 mm. and a bore of 18 mm. and has a thinner

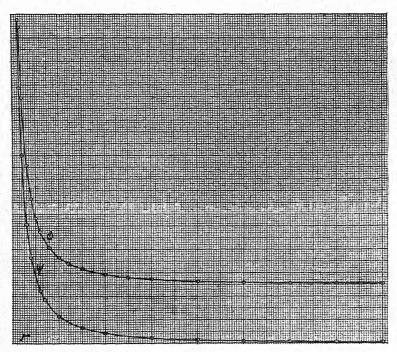


Fig. 1.

wall for its bore than almost any tube in practice. In fact none of the ordinarily used tubes can be treated as even very approximately "thin-walled." Simply to illustrate this point the necessary parts of Bradley and Browne's Table A has been reproduced in Table VII. The values of the breaking surface tension calculated from the data for r and P are given under T. Using these values of T as the limiting tension on the surface, the pressure P' required to produce

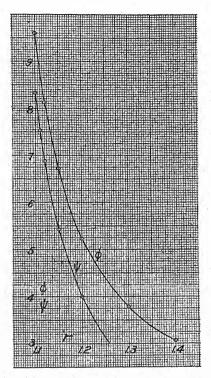


Fig. 2.

## TABLE VII.

No.	r	T	P.B W	P' for $r=3$ .
1	1.19	270	514	185
2	1.38	415	712	285
3	1.24	304	570	208
4	1.29	373	670	256
5	1.34	293	509	201
6	1.45	496	785	339

this tension when r=3, that is, for bore equal to wall, has been calculated and is given under P'. This will correspond with their calculated "norms" (PW/B). While they use their "norm" only

for comparison they state that it represents the bursting pressure of a tube where W/B=1. Their numbers are from 2.3 to 3.0 times greater than P'. Even for purposes of comparison the norm is not entirely satisfactory, a careful review of their data showing that when W/B increases the norm falls off. Except that they worked over such a narrow range of bore and wall this could not have escaped notice.

It will hardly need pointing out that this formula is of value largely for the purpose of calculating the required thickness of wall for a given bore and tensile strength to carry a given pressure. A factor of safety of at least 2 should be allowed even in the case of well-annealed tubes. For these calculations the curve  $\varphi$  will be found very serviceable. As pointed out by Bradley and Browne the wall thickness required is much less than ordinarily employed and it can be further pointed out that the extra wall thickness does not add nearly the strength usually expected.

The principal results of this paper are:

- 1. The testing of an excellent glass-metal joint.
- 2. The necessity for annealing commercial heavy-walled tubing to get the highest bursting strength.
- 3. The experimental proof of a formula for calculation of the tension on the inner surface at the bursting pressure, and the agreement of this with tensile strength.
- 4. For tubing where the wall thickness is greater than the bore, the bursting strength is practically independent of both bore and wall, and is approximately 1.3 times the tensile strength of the glass.
- 5. That no glass tubing in practical use should be treated as "thin-walled."
- 6. The use of the formula for calculating the required wall for a given tensile strength, bore and pressure.

Physical Laboratory,
University of Wisconsin,
November 10, 1908.

# THE TEMPERATURE COEFFICIENTS OF THE MOV-ING COIL GALVANOMETER.

By Anthony Zeleny and O. Hovda.

THE increasing use of the moving coil galvanometer for deflection work of precision renders a knowledge of its temperature coefficients desirable. The coefficients, however, differ greatly in different instruments so that no values can be determined which are applicable in general with any high degree of accuracy, but their nature and order of magnitude can be learned from the values that have been obtained for one type of the instrument.

As no similar determinations appear to have been published, the method employed in obtaining the values of the coefficients is described and the deductions are given at some length. This is done to show also some peculiarities of the instrument, which may not be generally known.

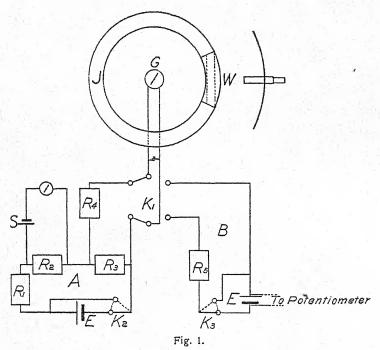
All observations were made on two galvanometers 1 having chilled cast-iron magnets.

# § 1. The Temperature Coefficient for Current Measurements.

The diagram of the apparatus employed for determining the temperature coefficient for current measurements is shown in Fig. 1. The galvanometer G was inclosed in a double walled jacket J, having a small window W for the taking of observations. The constancy of the temperature of the water circulating between the walls of the jacket was maintained automatically. The air surrounding the galvanometer was kept in motion by two fans operated by a small motor, and the temperature of the galvanometer was determined by means of a mercury thermometer. To insure that variations in the results were not due to manipulation in obtaining a constant current, two independent circuit arrangements were

Leeds and Northrup Co., "P Type."

employed as shown in the diagrams A and B of Fig. 1. These were connected to the galvanometer, in succession, by means of the commutator  $K_1$ . The current flowing through the galvanometer was maintained constant during each set of readings for all the observations taken at the various temperatures. When the circuit B was employed, the resistance  $R_5$  was 500,000 ohms when the upper suspension was of phosphor bronze and 300,000 ohms when it was of steel. This high resistance rendered negligible the change in



resistance of the galvanometer. When the circuit A was employed, the constancy of the main current was maintained by means of the resistance  $R_1$  and the secondary circuit containing the cadmium cell S, while the resistance of the galvanometer branch was maintained constant by altering the resistance in the box  $R_4$  to correspond to the known change in the resistance of the galvanometer.

The same galvanometer coil and lower phosphor-bronze spiral were employed in all determinations, while the upper suspension was either of phosphor bronze or of steel.

In the preliminary determinations it was found that between 0° and 60° C. the results obtained for the temperature coefficient were, to the limit of accuracy attained, independent of the temperatures employed.

The effect of thermo-electric currents was eliminated by taking the null readings while the keys  $K_2$  or  $K_3$  were turned so as to cut out the battery and leave the galvanometer circuit closed.

The observations and results obtained, when using a 3 mil phosphor-bronze suspension 13 centimeters in length, are given in Tables I. and II. The observations were taken on a circular scale at a distance of 50 centimeters.

TABLE I.

Galvanometer No. 6788. Phosphor-Bronze Suspension.

Tempe	ratures.	- Circuit.	Deflect	ions at	Difference.	Temperature
t'	t''	- Circuit.	t'	l"	Dinerence.	Deflections.
5.1	54.7	A	21.748	21.909	+ 0.161	+ 0.00015
5.2	54.7	В	18.539	18.634	0.095	.00010
54.7	5.2	A	21.894	21.748	0.146	.00014
54.7	5.1	В	18.631	18.532	0.099	.00010
4.9	54.4	A	18.454	18.590	0.136	.00015
5.0	54.4	В	18.420	18.545	0.125	.00014
54.4	5.0	A	18.593	18.472	0.121	.00013
55.4	5.0	В	18.560	18.430	0.130	.00014
				1.00		+ 0.00013

TABLE II.

Galvanometer No. 6737. Phosphor-Bronze Suspension.

Tempe	Temperatures.		Deflect	ions at	Difference.	Temperature Coefficient for	
- t'	t"	Circuit,	ť	t"	Difference.	Deflections.	
56.5	5.°0	. A	17.850	17.680	+ 0.170	+ 0.00019	
56.4	5.0	B	17.959	17.743	0.216	.00024	
34.7	14.8	A	17.791	17.717	0.074	.00021	
34.7	14.8	B	17.842	17.749	0.093	.00026	
18.8	44.2	A	17.738	17.853	0.115	.00026	
18.8	44.2	В	17.745	17.855	0.110	.00025	
44.3	20.6	A	17.861	17.775	0.086	.00020	
44.2	20.5	В	17.867	17.781	0.086	.00020	
						+ 0.00023	

The average of the above two values is assumed to be the approximate temperature coefficient for this type of galvanometer when its upper suspension is a 3 mil phosphor bronze strip. The expression for the relation of the deflections for equal currents at different temperatures then may be written

$$d'_{t} = d'_{20} \left[ 1 + 0.00018 (t - 20) \right]. \tag{1}$$

In Table III. are given the observations and results obtained for galvanometer No. 6788 when the upper suspension was a steel strip. The figure of merit at  $20^{\circ}$  was now  $5.48 \times 10^{-7}$  in place of  $2.26 \times 10^{-7}$  for the phosphor-bronze strip.

TABLE III.

Galvanometer No. 6788. Steel Suspension.

Temperatures.		Circuit.	Deflect	ions at	Difference.	Temperature Coefficient for	
t'	t''	Circuit.	t'	t"	Dincience.	Deflections.	
2.̈́7	53.7	Λ	12.702	12.706	+0.004	+0.00001	
2.5	53.9	В	12.695	12.692	-0.003	-0.00001	
53.7	3.5	A	12.672	12.671	+0.001	.00000	
53.9	3.6	B	12.679	12.677	+0.002	.00000	
		2,1				0.00000	

This shows that the temperature coefficient for this galvanometer with a steel suspension is practically negligible. See also calculated value of the coefficient for galvanometer No. 6737, in Table VIII, which makes the average value for the two galvanometers + 0.00005.

# Sources of Error.

The large variation in the individual results obtained when using the phosphor-bronze suspension are due to several causes:

- 1. Zero Shift. On changing the temperature, the null reading changed by an amount varying from two to ten millimeters. This introduced an error of unknown magnitude due to the change of position of the coil within the field and to the eccentricity of the scale. Precautions were taken to minimize this error as far as possible.
- 2. The assumption, based on the preliminary experiments, that the coefficient is the same at all temperatures is not strictly correct.

This is inferred from the variation of the temperature coefficient of the magnetic field, shown in Table VI.

- 3. Magnetic Hysteresis Due to Magnetic Impurities in the Coil.— Errors due to this were eliminated as far as possible by short-circuiting the galvanometer on the return of the coil to the null reading so as to render it aperiodic; also, while deflecting, the coil was damped by means of rapid tapping of the short-circuiting key so that it did not move beyond the point of the permanent deflection. See also § 5.
- 4. Molecular changes<sup>2</sup> within the suspension fiber may have changed the torsional moment with time.
- 5. The lag in the field strength of the magnet was eliminated by keeping the galvanometer at a constant temperature for about three hours before the observations were taken.

# § 2. Temperature Coefficient for Potential Measurements.

The temperature coefficient for potential measurements is determined from the deflection coefficient for current measurements and the resistance coefficient of the galvanometer circuit. The latter must be known for each particular case, for the galvanometer resistance is only a fraction of the total.

To enable the calculation of the resistance coefficient of galvanometers to be made, the coefficients of the suspension fibers, spirals, and the coil, were determined separately.

The following resistance equations were obtained:

For phosphor-bronze spirals or suspensions,

$$R_t = R_{20} [1 + 0.00063 (t - 20)].$$
 (2)

For steel suspensions, 
$$R_t = R_{20} [1 + 0.00356 (t - 20)].$$
 (3)

For the galvanometer coil, 
$$R_t = R_{20} [1 + 0.00394(t - 20)]$$
. (4)

In the galvanometer employed, the resistence of the upper phosphor-bronze suspension was 3.34 ohms at 20° C., and of the spiral, 17.25 ohms; that of the steel suspension was 5.71 ohms, and of the galvanometer coil, 96 ohms.

<sup>&</sup>lt;sup>1</sup> A. Zeleny, Phys. Rev., Vol. 23, p. 400, 1906.

<sup>&</sup>lt;sup>2</sup> K. E. Guthe, Bulletin of the Bureau of Standards, Vol. 2, p. 53, 1906.

Table IV.

Representing the resistance coefficient of the whole circuit by B, the deflections for equal differences of potential for the above galvanometer are derived from the following equations:

With phosphor-bronze suspension,

$$d_t = d_{20} [1 + (0.00018 - B) (t - 20)].$$
 (5)

With steel suspension, 
$$d_t = d_{20}[1 + (0.00005 - B)(t - 20)]$$
. (6)

§ 3. TEMPERATURE COEFFICIENT FOR BALLISTIC MEASUREMENTS.

The temperature coefficient for ballistic throws was obtained by discharging through the galvanometer, at different temperatures, equal quantities of electricity from a mica condenser charged by means of cadmium cells. The observations and results are given in

TABLE IV.

Galva- nometer.	Suspension.	Temperatures.		Throws at		Coefficient for
		ť	<i>t</i> "	ť'	t"	Ballistic Throws.
No. 6788	Phosphor-	54.0	4.0	18.491	18.708	-0.00023
	bronze.	54.2	5.3	18.082	18.254	-0.00019
						-0.00021
No. 6788	Steel.	2.6	53.8	12.310	12.179	-0.00021
		53.8	4.9	12.179	12.322	-0.00024
			15.7			-0.00022
No. 6737	Phosphor- bronze.					-0.000121

The value of the coefficient in the cases given is practically independent of the kind of suspension, but varies with the galvanometer employed. See also Table IX. The approximate temperature coefficients for ballistic measurements for this type of galvanometer having either a phosphor-bronze or a steel suspension, is assumed to be the average of the above values, and the relation of the ballistic throws for equal quantities at different temperatures is expressed by

$$d_t = d_{20} [1 - 0.00017(t - 20)]. \tag{7}$$

§ 4. CALCULATION OF THE TEMPERATURE COEFFICIENTS FROM THE COEFFICIENTS OF THE VARIOUS PARTS OF THE GALVANOMETER.

The temperature coefficients of a moving coil galvanometer are due to the variation of several quantities with temperature. The

<sup>&</sup>lt;sup>1</sup> The average of six independent sets of observations.

temperature coefficients of these quantities may be determined separately, and, from the relation of the temperature coefficients of the galvanometer to these coefficients, the former may be calculated from the latter. A comparison of the values obtained directly by experiment with those thus calculated gives an index to their reliability and shows the magnitude of the effect produced by the various causes which combined to produce errors in the observed results.

It was necessary to determine the temperature coefficients for the strength of the magnetic field and for the period of vibration of the coil system. The values of the expansion coefficients of the copper in the coil and of the iron in the magnet were taken from tables.

(a) The Temperature Coefficient for the Strength of the Magnetic Field. — To determine the variation in the strength of the magnetic field with the temperature, the coil was removed from the galvanometer, and the magnet and iron core were set forward from the wooden supporting frame a distance of about one centimeter. Two rectangular coils, each consisting of 45 turns of silk-covered manganin wire, were made to slide one on each side of the iron core, and were of such size and so placed that when withdrawn each loop cut all the lines of force once. These coils were connected in series with a ballistic galvanometer through the secondary of a standard mutual inductance coil, and the number of lines in the field, at different temperatures, was determined by comparison with this standard whose coefficient of mutual induction was 0.017653 henry. The current in the primary of the standard coil was measured by

TABLE V.

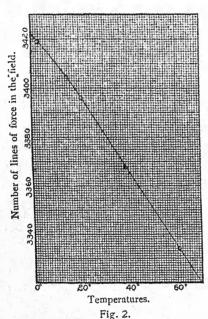
Current in Pri- mary of Standard Coil.	Throw from Standard Coil.	Throw Due to Cutting Field of Magnet.	Temperature of Magnet. Degrees.	Number of Lines of Force in the Field.
0.16669	18.784	19.642	2.9	3419.2
0.16702	18.837	19.575	14.8	3404.8
0.16655	18.782	19.524	20.9	3396.2
0.16652	18.768	19.350	38.8	3367.7
0.16590	18.672	19.130	60.6	3334.2

<sup>&</sup>lt;sup>1</sup> A. Zeleny, Phys. Rev., Vol. 23, p. 411, 1906; E. B. Rosa, Phys. Rev., Vol. 24 p. 241, 1907.

means of a potentiometer and standard resistance. The observations and results for the magnet of galvanometer No. 6788 are given in Table V.

These results are plotted in Fig. 2.

The average temperature coefficients for various ranges, as de-



termined from the curve, are given in Table VI. The temperature coefficients for the field strength were obtained from the temperature coefficients for the total number of lines and the expansion of the pole faces of the magnet.

The temperature coefficient for the field strength of galvanometer No. 6737 between 15° and 30° C. was found to be —0.00035, the total number of lines at 20° C. being 3,172. The area of each pole face was 8 sq. cm.

(b) Temperature Coefficient for the Time of Vibration of the Coil. — The temperature coeffi-

cient for the time of vibration was obtained with the coil both outside and within the field of the magnet. The results are given in Table VII.

TABLE VI.

Range of Temperature.	Temperature Coefficient for the Number of Lines.	Temperature Coefficient for the Field Strength.
0° to 20° C.	-0.00037	-0.00039
20° to 40°	-0.00046	-0.00048
40° to 60°	-0.00046	-0.00048
0° to 60°	-0.00043	-0.00045
15° to 30°	-0.00044	-0.00046

The difference in the values of the coefficient, within and without the field, is due to the presence of magnetic impurities within the coil.

TABLE VII.

Galvanometer.	Suspension.	Coil Outside of Magnetic Field.	Coil Within the Magnetic Field.
No. 6788	Phos. bronze.	+0.00027	+0.00032
""	Steel.	+0.00021	+0.00023
No. 6737	Phos. bronze.		+0.00031

(c) Calculation of the Coefficient for Current Measurements. — From the equation for the time of vibration of the coil

$$t = 2\pi \sqrt{\frac{I}{T+M}},$$

$$\frac{(T+M)_t}{(T+M)_{20}} = \frac{t_{20}^2 I_t}{t_t^2 I_{20}} \equiv \frac{t_{20}^2 D_t^2}{t_t^2 D_{20}^2},$$
(8)

where T, M, t, I, D, are respectively the torsional moment, magnetic moment due to impurities, period of vibration, moment of inertia, and the width of the coil. The subscripts represent temperatures.

Assuming the field to be practically uniform, the relation between the current and the deflection is expressed by

$$\frac{1}{10}FLnDi\cos\theta \equiv (T+M')\theta = (T+M')kd',$$
 (9)

where F, i, d', M', represent respectively, the strength of the magnetic field, the current, the deflection, and the moment due to the magnetic impurities, which may differ somewhat from M. The effective length L of the coil does not vary with the expansion of the copper, for both ends of the coil extend beyond the field of the magnet, but does vary with the linear expansion of the iron of the magnet.

From equations (8) and (9), assuming  $(T+M) \equiv (T+M')$ ,

$$\frac{d_t'}{d_{20}'} = \frac{D_t F_t L_t (T+M)_{20}}{D_{20} F_{20} L_{20} (T+M)_t} = \frac{F_t t_t^2 L_t D_{20}}{F_{20} t_{20}^2 L_{20} D_t}, \tag{10}$$

from which

$$d_k' \equiv F_k + 2t_k + L_k - D_k, \tag{II}$$

where  $d_{s}$ ,  $E_{s}$ ,  $t_{s}$ ,  $L_{s}$ .  $D_{s}$  are the temperature coefficients respectively for the deflections, field strength, time of vibration, linear expansion of cast iron and that of copper,

The calculations and comparisons are made in Table VIII.

440			90.166
I A	BLE	$-\mathbf{V}\mathbf{I}$	11

nometer.	Suspension.	F	21.	Lam Da	Temp, Coef. fo	r Deflections
			land the		Calculated.	Observed.
No. 6788	Phos. bronze,	0.00045	0.00064	-0.00001	+0.00018	+0.00013
Na. 6737	44	-0.00035	+0.00062	-0.00001	+ 0.00026	+0.00023
					+0.00022	+0.00018
No. 6788	Steel.	-0.00045	0.00046	-0.00001	0.00000	0.00000
No. 6737		-0.00035	$(\pm 0.00046)$	-0.00001	+0.00010	4.0
		1		\$ 1.	+0.00005	100

(d) Calculation of the Coefficient for Ballistic Throws.—From the equation for the constant for ballistic measurements,  $K = K't \sqrt{\rho/2\pi}$ , the relation between the deflections for equal quantities at different temperatures is, for open circuit work where  $\sqrt{\rho}$  is small, expressed by

$$\frac{d_t}{d_{20}} = \frac{K_{20}}{K_t'} = \frac{K_{20}'t_{20}}{K_t't_t} = \frac{d_t't_{20}}{d_{20}'t},\tag{12}$$

where d, d', and t, represent ballistic throws, deflections for continuous currents, and periods of vibration, at the temperatures  $t^o$  and  $20^\circ$  C. From this

$$d_k \equiv d_k' - t_k, \tag{13}$$

where  $d_k$ ,  $d_k'$ , and  $t_k$ , represent the temperature coefficients respectively for the ballistic throws, deflections for continuous currents, and the periods of vibration. The calculations and comparisons are made in Table IX.

The agreement of the calculated with the observed values, in Tables VIII, and IX., is as close as can be expected when the sources of error given in \$1 and \$5 are considered; in addition to these sources of error it was necessary, in \$4 (c), to assume the magnetic moment due to the impurities in the coil to be the same whether the coil is vibrating or is deflected and at rest.

TABLE IX.

Galva- nometer.	Suspension.	$d_{k'}$	$-t_k$	Temp. Coef.	for Ballistic
No. 6788			-	Calculated.	Observed.
No. 6788	Phos. bronze.	+0.00013	-0.00032	-0.00019	-0.00021
No. 6737		+0.00021	-0.00031	-0.00010	-0.00012
				-0.00015	-0.00017
No. 6788	Steel.	0.00000	-0.00023	-0.00023	-0.00022
No. 6737	"	+0.00010	-0.00023	-0.00013	1 2 2 2 2
			A 1	-0.00018	

### §5. Magnetic Impurities within the Coil.

- I. The galvanometer coil, on open circuit, was suspended between the poles of an uncharged electromagnet, and when the latter was charged, the coil turned through a considerable angle toward parallelism with the lines of force, showing the presence of magnetic impurities.
- 2. A galvanometer coil, on open circuit, turns on its axis when the magnetic field of the galvanometer is short-circuited. This also shows the presence of a directive moment due to magnetic impurities in the coil. When the field is weakened, the directive moment of the impurities is lessened and the coil is allowed to return nearer to the position it would occupy if there were no impurities. In twelve galvanometers in which the fields were short-circuited, the coils turned through angles represented by deflections varying from a few tenths to several millimeters on the scale. In one case only was there no appreciable deflection.
- 3. The restoring moment in a vibrating galvanometer coil is produced in part by these magnetic impurities within the coil. The value of the restoring moment due to the impurities as compared with the torsional moment of the suspension was determined from the periods of vibration of the system when in the magnetic field and when outside of it. The ratio of M/T is then obtained from

$$t = 2\pi \sqrt{\frac{I}{T+M}},$$

where T and M represent respectively the torsional and magnetic

moments per unit angle of displacement. The magnetic moment produced by the earth's magnetic field acting on the magnetic impurities was considered negligible. The observations and results are given in Table X.

TABLE X.

Field.	Period of Vibration.	M) T
Earth's field.	8.534"	(0.00)
Galvanometer magnet.	8.289	0.07
Strong electromagnet.	6.03	1.00

The results show how large a part the magnetic impurities play in the directive action upon the coil and how much they diminish the sensitiveness of the galvanometer.

4. The deflection, in the particular galvanometer employed, changed about one tenth of a millimeter during the first minute after the coil came to rest immediately following a previous deflection in the same direction. On account of the large influence of the magnetic impurities, this may be ascribed to the lag in the change of direction and strength of the magnetism in the magnetic impurities rather than to a change in the torsional moment or the fatigue of the suspension.

The above considerations help to explain the irregularities in the results obtained for the temperature coefficients. The hysteresis of the magnetic impurities and the effect of temperature upon them must produce disturbing effects.

#### § 6. SUMMARY AND DISCUSSION.

The moving coil galvanometer has three temperature coefficients, one each for current, potential, and ballistic measurements. On account of magnetic hysteresis and other disturbing causes, it was found impossible to determine the values of these coefficients for an individual instrument with as high a degree of precision as it is possible to read deflections or throws. The values of the coefficients for different galvanometers of the same construction and materials, are found to differ considerably, so that only approximate values can be given for any type of the instrument.

The averages of the sets of values obtained for the two galvanometers are taken as the approximate temperature coefficients for all moving coil galvanometers having chilled cast-iron magnets. These values are summarized in Table XI., where B, as before, represents the temperature coefficient for the resistance of a particular circuit.

TABLE	ΧŢ
TUDLE	~XX.

Kind of Measurement.	Suspension.	Temperature Coefficient.
Current.	Phos. bronze (3 mil).	+0.00018
	Steel.	+0.00005
Potential.	Phos. bronze (3 mil).	+0.00018-B
"	Steel.	+0.00005-B
Ballistic.	Phos. bronze (3 mil).	-0.00017
	Steel.	-0.00017

These values are very nearly correct for galvanometers whose magnets have a field intensity of 425 units and a temperature coefficient of -0.00040, and in which M/T = 0.07 approximately.

The influence of a variation in the value of M/T upon the temperature coefficient of the galvanometer can be estimated from the difference in the temperature coefficients for the time of vibration within and without the field, given in Table VII. The value of the temperature coefficient for the time of vibration with the 3 mil phosphor-bronze fiber is 0.00005 larger within than outside the field. If there were no magnetic impurities in the coil, or, more correctly, if the amount of the magnetic impurities present was just sufficient to neutralize the effect due to the diamagnetic properties of the copper, the temperature coefficient for the time of vibration in the field of the magnet would be the same as that determined without the field. In such a case, as is seen from equation (II) and in Table VIII., the temperature coefficient for current measurements would be obtained by subtracting 0.00010 from the value given in Table XI., and the temperature coefficient for ballistic throws by adding - 0.00005 to the corresponding value.

With a 1.5 mil phosphor-bronze suspension, M/H was found to have a value of 0.9 and the temperature coefficient for the time of vibration a value of + 0.00039 in the field of the galvanometer magnet. The latter value gives for the temperature coefficient of the galvanometer for current measurements a value of + 0.00032 and for ballistic throws a value of - 0.00007.

It is inferred from the values of the temperature coefficients for the

total number of lines obtained by B. O. Peirce i for several chilled cast-iron magnets, that the temperature coefficient for the field strength of any particular magnet of this type is not liable to exceed much the limits of the two here used.

The temperature coefficients of a galvanometer with a magnet other than chilled cast iron can be calculated from the known temperature coefficient of its field strength by the aid of equations (11) and (13) and the values given in Table XI. If  $F_k$  be the value of the temperature coefficient of the field strength of any galvanometer magnet and K represents any one of the temperature coefficients of the galvanometer with a chilled cast-iron magnet, the value of the corresponding temperature coefficient for a galvanometer with the former magnet is represented by

$$K' = K + (F'_k + 0.00040),$$
 (14)

where the proper algebraic signs for K and  $F_k'$  must be used. The temperature coefficients of the field strengths for magnets made of various materials can be computed from the temperature coefficients for the total number of lines, determined for such magnets by B. O. Peirce in the paper cited above.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
Nov. 27, 1908.

<sup>1</sup>Proceedings of Am. Acad. of Arts and Sciences, Vol. 38, p. 551, 1903; Vol. 40, p. 701, 1905.

# THE ABSORPTION AND REFLECTION OF CALCITE AND ARAGONITE FOR INFRA-RED RAYS AS DEPENDENT UPON THE PLANE OF POLARIZATION.<sup>1</sup>

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THE structure and vibration periods of molecular aggregations would naturally first be sought in compounds of simplest composition. Certain groups of atoms having particular free periods by themselves may lose these periods when related in a complicated manner. Previous investigations in the infra-red of absorption and reflection spectra have shown that each of the simple compounds of the same acid radical, viz., nitrates, sulphates and carbonates have characteristic bands in the same regions of the spectrum. The carbonates, as demonstrated by Morse,<sup>2</sup> show reflection maxima in the infra-red, the positions of which vary with the atomic weight of the base in an approximately straight line relation.

The most direct method of attacking the question of molecular structure is through the behavior of crystalline media, since the vibrations are limited to definite directions in the crystal. Little has been done in this direction, in part for the want of a suitable polarizer for long waves, and largely because of the loss of energy by polarization. As regards selective reflection as dependent upon the plane of polarization, the field is new.

That absorption in doubly refracting media is dependent upon the direction of vibration of the incident energy has been demonstrated conclusively by the work of Merritt<sup>3</sup> and of Königsberger.<sup>4</sup> In the case of calcite the independence of the absorption for the

<sup>&</sup>lt;sup>1</sup>Presented by title at the Washington meeting of the American Physical Society, April 24–25, 1908. Abstracted in the Physical Review, 26, 539, 1908.

<sup>&</sup>lt;sup>2</sup> Astrophys. Jour., 11, 225, 1907.

<sup>&</sup>lt;sup>3</sup> Phys. Rev., 2, 424, 1895.

<sup>&</sup>lt;sup>4</sup> Ann. der Phys., 61, 687, 1897.

ordinary and extraordinary rays was especially marked. The work was not carried beyond 5.5  $\mu$ , due to the loss of energy by polarization.

The identity of composition of calcite and aragonite together with the differences in crystallographic structure of the two substances, suggested them as worthy of further investigation. The large differences in the indices of refraction for two of the principal directions of vibration of both calcite and aragonite, and the simplicity of composition, would hint that large differences in absorption and reflection might be expected.

The work of this investigation consisted of two parts, dealing respectively with the absorption and reflection spectra for the principal directions of vibration of calcite and aragonite.

#### DESCRIPTION OF APPARATUS.

A diagram of the apparatus as arranged is shown in Fig. 1.

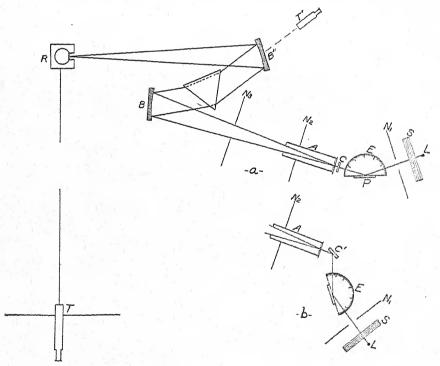


Fig. 1.

For the transmission spectra the collimating arm A of the spectrometer carried an attachment as indicated in a; for the reflection curves, this attachment was modified as shown in b.

Absorption. — Rays from a Nernst heater L fell upon the polarizer P from which they were reflected into the slit of the spectrometer, and after reflection from the concave minor B passed through the prism and were brought to a focus upon the radiometer R by the second concave minor B'. Deflections were produced by raising the shutter S. The crystal section, whose transmission spectrum was desired, was placed at C. The crystal was mounted on a simple mechanism permitting it to be thrown in the path of the rays, always in the same position.

Reflection. — The same polarizing device used for the absorption work, was also used for the reflection curves as shown in b. Rays from the polarizer P were reflected to C', and from there to the spectrometer slit. The device at C' carried the crystal section attached to one of two arms, which turned about a common center. To the other arm was fastened a silver mirror for comparison. Either arm, when turned into position, dropped into a notch, pressing the reflecting surface against a fixed guide, which brought it to the same position for each observation.

The arm carrying the source L could be turned about the center of the graduated arc E as axis. The polarizer was attached rigidly to this graduated arc, the combination being free to turn about its center.

The scale T was placed 120 cm. from the radiometer.

Spectrometer. — The reflection spectrometer had a focal length of 35 cm. The method of constant angle of emergence was employed, so that the source and likewise the devices for polarization, absorption and reflection were attached rigidly to the collimating arm. These attachments could produce no strain in the instrument since the whole weighed less than one-half kilogram. The rock-salt prism was the same one used by Coblentz during his investigations in this laboratory. As no changes in the prism faces had been made since that time, his calibration curve was used by the author also. The prism faces were 7 cm. square, and the refracting

<sup>&</sup>lt;sup>1</sup> Investigations of Infra-red Spectra, 16.

angle 59° 57′ 43″. A circular plate of glass somewhat larger than the dimensions of the prism was cemented on the prism table. Upon this plate the prism was accurately mounted. A small beaker containing phosphorus pentoxide was placed on the prism to absorb moisture. A bell-jar attached to a weighted cord, passing over a pulley above, could be lowered over the prism without jar to the apparatus and fit tightly upon the glass plate.

The angle of emergence was the angle of minimum deviation for sodium light. This angle was determined by the use of a telescope, Fig. 1, T', set up in line of the deviated rays from the prism. The collimating arm was first clamped at a convenient point on the spectrometer circle. The image of the slit was focused on the graduated scale of the eyepiece and the prism table adjusted to the angle of minimum deviation. The other arm of the spectrometer was then turned in position and adjusted until the image fell upon the radiometer slit. The settings were further checked by the position of the  $\mathrm{CO}_2$  band, from a bunsen burner, which falls sharply on 4.40  $\mu$ .

Radiometer. — A Nichols radiometer used by previous observers in this laboratory, was at hand. Several improvements, however, were added. The sensitiveness of the radiometer was determined in a former investigation. With a candle and scale at one meter distance a deflection of 12.5 centimeters per square millimeter of exposed vane area was produced.

Vanes. — The superiority of platinum black as an absorbent of radiant energy has long been recognized. To obtain a uniform electrolytic deposit without the added weight of metallic vanes, the following method was successful. Thin sheets of mica were platinized on one side with platinum chloride. The PtCl<sub>4</sub> was applied to the surface with a soft brush and allowed to dry. The mica was then heated over a metal plate until a thin layer of platinum appeared. This process was repeated several times until a uniform conducting layer was formed. In order that the platinum stick to the mica, it is essential that the surface of the mica be roughed with medium emery paper before the PtCl<sub>4</sub> is applied. Sheets of mica thus prepared were coated with platinum black after the electrolytic process of Kurlbaum.<sup>1</sup> The vanes were 1 × 11 mm. and the sus-

<sup>1</sup> Ann. der Phys., 67, 846, 1899.

pended system weighed o mg. The mirror was plane, about  $2 \times 3$  mm. The surfaces were ground, and the image was perfect. The fiber which was about 4.7 cm. in length, was attached to the bottom of a stirrup carrying a small bar magnet one centimeter long. This stirrup was attached with a short silk fiber to a support at the top of the radiometer chamber. Around the neck, leading from the radiometer, was a movable collar carrying a control magnet, which had first been bent into shape so its poles would lie in the plane of the suspended magnet. This device offered most excellent control of the suspended system. A double rock-salt window was set back just in front of the vanes. The slit was set back to the front surface of the window, so that the loss in definition of the image between the slit and the vanes was reduced to a minimum. The device carrying the slit rested in two guides on the front of the radiometer, allowing lateral adjustment. The width of both the radiometer and spectrometer slits was equal. For all observations from 1.7  $\mu$  to 9.8  $\mu$  this width was .3 mm., equivalent to 3' of arc on the spectrometer circle. For observations beyond 9.8  $\mu$ , the slits were widened to .55 mm., or 5.5' of arc. The time for a single deflection varied from .5 to 1.5 minutes when the radiometer was worked at its greatest sensibility. For observations in the more intense part of the spectrum the pressure was lowered until the radiometer acted ballistically. The time of deflection was thus reduced to 20 seconds. Within the tube leading from the radiometer was placed absorbent cotton mixed through with gold foil to absorb mercury vapor from the pump; no trouble from electrification of the vanes was experienced (see Coblentz).1

Source.—A Nernst heater operated on a well regulated 110 volt direct current circuit furnished the source of energy. The heater was run somewhat above its rated voltage and served as a very satisfactory source.

*Polarizer.* — Selenium, as shown by Pfund,<sup>2</sup> has the properties necessary for a good reflection polarizer for long waves. Pfund's investigations were carried to 13  $\mu$ ; however, it was found in the present investigation to reflect uniformly beyond 15  $\mu$ . A reflect-

<sup>&</sup>lt;sup>1</sup>Investigations of Infra-red Spectra, Appendix III., 124.

<sup>&</sup>lt;sup>2</sup> Astrophys. Journ., 1, 23, 1906.

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ing polarizer was made after this method, and polarization was complete. The angle of polarization was determined experimentally with a Nicol's prism. This angle, as measured on the device of Fig. I, was 71.5°.

Crystal Sections. — Polished sections cut by Zeiss from clear crystals of calcite and aragonite, and containing the principal directions of vibration, were employed. The section of calcite was 1 mm. thick, and cut parallel to the optic axis. The two aragonite sections were cut parallel to the ab and ac axes respectively. Large untwinned crystals of aragonite are difficult to obtain. The crystals examined were of the Bohemian type and of clear quality. The thickness of these plates was 2 mm., and the smaller one was about 1 cm. square. For a more definite location of the calcite bands of absorption than could be gained from the above section on account of its thickness, a thin section of calcite, .14 mm. in thickness, cut 70° to the optic axis, was also examined. The curves of this section serve well to show the great differences of absorption as dependent upon thickness.

A shutter consisting of five parallel plates of tin rendered radiation from the source through the shutter quite impossible. The plates of tin were placed about .5 cm. apart, permitting free circulation of air between them. The shutter was fastened from the ceiling and was operated with a cord by the observer. Observations were made in a small basement room completely surrounded by other rooms, and for this reason the temperature changes were very small. The spectrometer and radiometer were mounted on a table which itself stood on marble blocks imbedded in saw-dust, in boxes resting on the concrete floor. Very little trouble was experienced from tremors. Every precaution was taken to protect the apparatus from outside radiations. Both spectrometer and radiometer were completely covered. As a further protection to the spectrometer from direct radiations of the source, opaque screens were placed at N<sub>1</sub>, N<sub>2</sub>, N<sub>3</sub>. The source, polarizer, and slit were also screened from external radiations. The radiometer was kept connected with the mercury pump, but the stop-cock was always closed except during adjustments for sensibility, to prevent the diffusion of mercury vapor to the radiometer. All connecting joints were mercury sealed and little trouble with leaks was experienced.

#### METHOD OF OBSERVATION.

The same crystal sections were used for both the absorption and reflection curves. The fraction or percentage of transmission was the ratio of the deflection when the crystal was placed in the path of the polarized rays to the deflection when it was removed. Likewise, the reflection percentage was the ratio of the reflection from the crystal to that of silver assumed 100 per cent.

The plane of the polarizer was placed in a vertical position. A vertical strip of the reflecting surface about I cm. wide was used, the remaining part of the surface being screened with black paper. According to the theory of Fresnel, the direction of vibration of the polarized energy would also be in a vertical plane. The particular crystal direction to be examined was placed parallel to the direction of vibration of the incident energy.

The planes of polarization of these substances, as determined by the crystallographic axes, may be further defined as follows: The axis  $\alpha$  is the direction of least elasticity and greatest index of refraction, and a normal to the plane of the optic axes. The b direction is the obtuse bisectrix of the crystal, and the direction of medium elasticity and medium index of refraction. The c direction is the acute bisectrix, and the line of greatest elasticity and least index of For calcite the c axis is parallel to the optic axis. The refraction. a and b axes are equal.

All observations were repeated one or more times in parts of the spectrum where the energy was large, and usually six to eight times when the deflections were small. In each case the zero was determined by the mean of two readings, one before, and one after each deflection. With the crystal in position, the zero was noted at the instant the shutter was raised. When the mirror came to rest, the deflection was read and the shutter lowered; the crystal was turned out of the path of the energy and a second zero read, and at the same time a second exposure made after which the zero was again read. The middle zero was used in determining the mean zero of the two deflections. Before starting the observations, it was necessary to remain in the room at least a half hour until the temperature conditions became constant. With the excellent definition of the image of the scale, deflections were readily esti-

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mated to tenths of a millimeter. Recorded results are the means of all observations.

Due to deterioration of the silvered surfaces, two comparison mirrors were used for the reflection curves, viz., from 1.7  $\mu$  to 9.8  $\mu$  and 9.8  $\mu$  to 14.5  $\mu$  respectively. In each case special care was taken to secure the best polished surface.

#### RESULTS.

In the present investigation the curves of absorption and reflection for the principal directions of vibration of calcite and aragonite have been carried beyond the absorption and reflection bands at 14.2  $\mu$ . All curves have been drawn to the same scale in Figs. 2 to

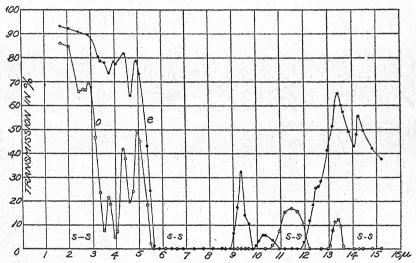


Fig. 2. Transmission curves for calcite (CaCO<sub>8</sub>), thickness 1.0 mm. o, ordinary ray; e, extraordinary ray; s-s, width of slit.

4, and 7 to 9. The reflection bands have been drawn to twice this scale of wave-length in Figs. 5 and 6, and 10 to 13.

Calcite. Transmission. — Observations were first made on the section of 1 mm. thickness. The ordinary ray (Fig. 2, o) shows a shallow absorption band at 2.46  $\mu$ . Strong bands are present at 3.46  $\mu$ , 3.96  $\mu$  and 4.58  $\mu$ . The section becomes opaque at 5.54  $\mu$  and continues to 10.52  $\mu$ . The ray is again completely absorbed from 12.2  $\mu$  to 13.0  $\mu$ , and beyond 13.63  $\mu$ .



The extraordinary ray (Fig. 2, e) indicates absorption bands at 3.74  $\mu$  and 4.65  $\mu$  and becomes opaque at 5.61  $\mu$ , continuing opaque to 8.83  $\mu$ . Another band falls sharply at 9.80  $\mu$ . The ray is also completely absorbed between 10.9  $\mu$  and 11.8  $\mu$ . The percentage transmission rises to 65.0 per cent. at 13.40  $\mu$ . A small absorption band falls sharply at 14.06  $\mu$ .

These results were compared with the work of Coblentz¹ who determined the transmission spectrum of calcite with unpolarized rays from 1  $\mu$  to 14.2  $\mu$  with a crystal section .14 mm. in thickness cut 70° to the optic axis. The curves for the two sections were so different that little relation could be established between them. Further, in comparing this curve with the curves of Merritt there seemed to be greater discrepancies. The specimen of Coblentz being cut 70° to the optic axis contains a predominance of the ordinary vibration, and its transmission curve should agree the closer with that of the ordinary ray, but the reverse relation was quite evident. An exactly similar section cut 70° to the axis was obtained and its transmission spectra plotted for the two planes of

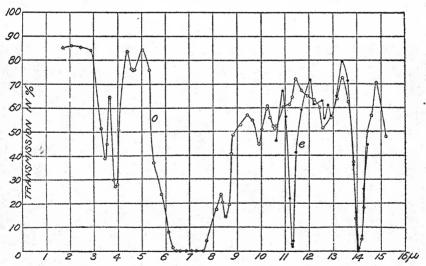


Fig. 3. Transmission curves for calcite, thickness 0.14 mm. o, ordinary ray; e, extraordinary ray.

polarization. The results from this section (Fig. 3) showed that the work of Coblentz was correct to 14  $\mu$ , and the differences exist-

<sup>1</sup> Investigations of Infra-red Spectra, Part III., 7.

ing for the two sections in question were accounted for entirely by difference in thickness. Likewise the seeming discrepancy with Merritt's work was readily explainable on this ground. The width, as also the depth of absorption bands increases with the thickness of the section so that for thin sections certain small bands completely disappear. The curve of the ordinary ray (Fig. 3, 0) represents the pure absorption of this ray, but for the extraordinary ray (Fig. 3, e) the results are slightly masked by the behavior of the ordinary ray. The principal bands of the ordinary ray between  $2 \mu$  and  $6 \mu$  for both sections agree. The broad band of complete absorption in the region of 7  $\mu$  lies within the limits 6.36  $\mu$  to 7.60  $\mu$  for the thin sec-The bands at 8.50  $\mu$ , 9.92  $\mu$  and 10.57  $\mu$  are not brought out by the thick section. These curves show conclusively that the absorption band at 11.3  $\mu$  is due entirely to the absorption of the extraordinary ray. There is no trace of an absorption band in this region for the ordinary ray. At 12.66  $\mu$  a band is present in both

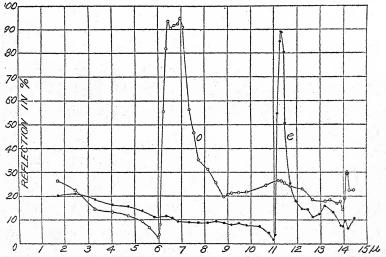


Fig. 4. Reflection from calcite. o, ordinary ray; e, extraordinary ray.

rays. The point of maximum transmission occurs at 13.4  $\mu$  for both rays and the transmission for the two is not very different. But the curves of Fig. 2 serve well to show that the coefficient of absorption in this region is much greater for the ordinary ray than for the extraordinary ray. The ordinary ray is completely absorbed

at 14.06  $\mu$  while the extraordinary ray shows only a shallow band in this region for the thick section. Due to the component which the ordinary ray exerts in the thin section, the extraordinary ray will show the band at 14.06  $\mu$  much exaggerated in depth. The positions of the absorption bands of calcite are given by Kayser as follows: 6.69  $\mu$ , 11.41  $\mu$ , 14.4  $\mu$  and 29.4  $\mu$ . In the present investigation, if the center of the first band be taken as 6.71  $\mu$ , the variations from the above values are + .02  $\mu$ , - .11  $\mu$  and - .3  $\mu$  respectively.

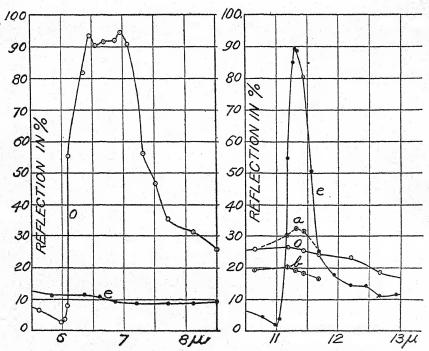
Reflection. — The reflection curves for calcite have relations similar to the absoption curves. The first reflection band occurs in the ordinary ray (Fig. 4, o). It is broad and complex, with two principal and nearly equal maxima at  $6.46~\mu$  and  $6.96~\mu$ , and indication of another maxima at  $6.70~\mu$ . This band is no doubt more complex than indicated in this curve. Coblentz  $^2$  with unpolarized energy found a complex reflection band for calcite with maxima at  $6.5~\mu$  and  $6.6~\mu$ , and a complex maximum in the region of  $7~\mu$ . The absence of any absorption band at 11.3  $\mu$  in the transmission curve of the ordinary ray is likewise brought out by the absence of a reflection band in this region for the ordinary ray.

For the extraordinary ray (Fig. 4,  $\epsilon$ ) which showed complete absorption in the regions 6.7  $\mu$  and 11.3  $\mu$  for the thick section, there undoubtedly would have been complete absorption in the latter region by the thin section, except for the direction in which the crystal was cut. This ray shows no trace of a reflection band at 6.7  $\mu$ , but a very strong band, reflecting 89.1 per cent. of the incident energy at 11.30  $\mu$ . The position of this band from the transmission curve is 11.28  $\mu$ . This small difference might readily be explainable again by the impurity of the extraordinary curve. As shown in Fig. 3, the ordinary curve is changing very rapidly in this region and in a manner to shift the minimum toward the shorter wave-lengths. Both curves exhibit reflection bands beyond 14  $\mu$ . For the extraordinary ray in which absorption was not complete, the change in reflection is also small, and coincides in position with the absorption band. The ordinary ray is com-

<sup>&</sup>lt;sup>1</sup> Handbuch der Spectroscopie, Vol. IV., 502.

<sup>&</sup>lt;sup>2</sup> Supplementary Investigations of Infra-red Spectra, Part V., 23.

pletely absorbed at  $14.06 \,\mu$  but its reflection band is shifted to  $14.17 \,\mu$ . The importance of exact setting of the crystal is brought out by the broken curve a, Fig. 6. This band, since it was not a typical reflection band, led to a question of error in setting the crystal, or incompleteness of polarization. The crystal was reset with



Figs. 5-6. Reflection from calcite. o, ordinary ray; e, extraordinary ray.

greater exactness and this region reëxamined. The full curve  $\mathbf{r}o$  was obtained. To check this point further another section cut perpendicular to the optic axis was investigated through this region. In this curve there could be little possibility of the extraordinary ray exerting an influence, and for this crystal the broken curve b, Fig. 6, was obtained, checking the curve o.

Aragonite. Transmission. — When the direction of vibration of the incident energy is parallel to the a axis (Fig. 7, a) the curve is not very different from the ordinary curve for calcite. The first band appears as 2.46  $\mu$ , another at 3.30  $\mu$ , and then a band of zero

transmission at 4.04  $\mu$ . At 5.54  $\mu$  there is complete absorption continuing to 9.50  $\mu$ . This direction transmits very little energy in the region 9.5  $\mu$  to 12.0  $\mu$ . At 13.92  $\mu$  the curve falls to zero and continues to the end of the observations.

The curve for the second direction of vibration (Fig. 7, b), parallel to the b axis, is somewhat similar to the transmission curve a, but

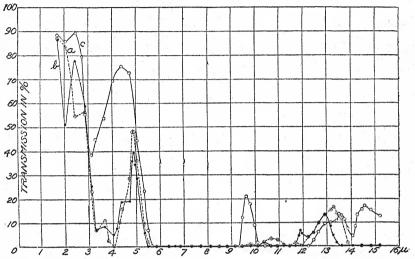


Fig. 7. Transmission curves for aragonite (CaCO<sub>3</sub>), thickness 2.0 mm.  $\alpha$ , vibrations  $\parallel a \perp b$  axis; b, vibrations  $\parallel b$  axis; c, vibrations  $\parallel c$  axis.

shows a shift toward the shorter wave-lengths of some of its maxima and minima. Absorption bands are present at 2.05  $\mu$ , 3.30  $\mu$  and 4.04  $\mu$ . The absorption is complete from 5.45  $\mu$  to 10.10  $\mu$ , and again between 10.6  $\mu$  and 11.7  $\mu$ . Another band appears at 12.20  $\mu$ , and beyond 13.5  $\mu$  the transmission is zero.

When the incident vibrations are parallel to the c axis (Fig. 5, c) the transmission curve resembles the extraordinary curve for calcite. This resemblance is especially close in the region  $9 \mu$  to  $15 \mu$  except that the transmission maxima and minima in the aragonite curve are shifted about .25  $\mu$  toward the longer waves in all cases except the band at 14.06  $\mu$ , for which there is exact coincidence. From 1.7  $\mu$  to 5.5  $\mu$  this curve shows a greater transmission of energy than curves a and b. In this region there is a shallow band at 2.05  $\mu$  and a deep band at 3.13  $\mu$ . Absorption is complete from

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5.65  $\mu$  to 9.32  $\mu$ . Again there is opacity from 10.13  $\mu$  to 12.26  $\mu$ . A sharp absorption band falls at 14.06  $\mu$ .

According to the theory of the ellipsoid of elasticity, the optical properties of a crystal are dependent upon the displacement of the particle in the direction of vibration, and independent of the ray direction through the medium. The two sections of aragonite contained four principal directions of vibration, two of which were parallel to the common axis a. As a further check upon the work in hand and to demonstrate that in a biaxial crystal absorption is dependent only upon the direction of vibration, the absorption curves for the directions a, a in the two sections were obtained (Fig. 8). The

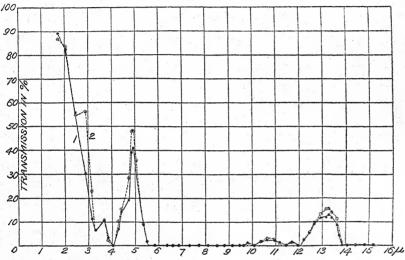


Fig. 8. Transmission curves for aragonite, thickness 2.0 mm. I, vibrations  $\parallel a \perp c$  axis; 2, vibrations  $\parallel a \quad b$  axis.

ray directions through the crystal in the two cases were normal to each other, but the directions of vibration parallel. The two curves show that the absorption characteristics are very similar. For curve 1, the ray direction was parallel to b, and parallel to c for curve 2. The difference of note is the band at 2.46  $\mu$  which occurs in curve 2, but is entirely absent in 1. In most parts the transmitting power of 2 is greater than 1.

Reflection. — When the incident energy is parallel to the a axis (Fig. 9, a) nearly 100 per cent. of this energy is reflected at 6.65  $\mu$ .

It is universally true that substances showing powerful selective absorption also exhibit correspondingly large reflecting powers in the same regions, yet few substances reflect so powerfully as this. Because of the sharpness and high reflecting power of this band, its

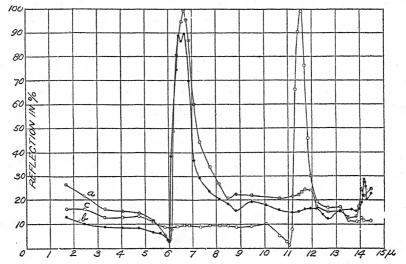


Fig. 9. Reflection from aragonite. a, vibrations  $\parallel a \perp c$  axis; b, vibrations  $\parallel b$  axis; c, vibrations  $\parallel c$  axis.

maximum must necessarily determine the position of the absorption maximum for this ray. No band is present at 11.55  $\mu$  for this direction. Its second band falls at 14.06  $\mu$  and through this region absorption was complete for the corresponding transmission curve.

In the second reflection curve (Fig. 9, b) the direction of vibration is parallel to the b axis. This curve has a complex band in the first region. The band has two sharp and nearly equal maxima which fall at 6.46  $\mu$  and 6.70  $\mu$  respectively. Coblentz, with unpolarized energy, found a complex reflection band for aragonite with two maxima at 6.53  $\mu$  and 6.75  $\mu$  respectively. The first maxima of the complex band of calcite occurs also at 6.46  $\mu$ . There is no band at 11.55  $\mu$ , but at 14.17  $\mu$  a sharp band is present with a reflecting power of nearly 29 per cent. The transmission curve for this ray also shows opacity in this region. The position

of this band agrees exactly with the corresponding band for the ordinary ray of calcite.

For the third curve the direction of vibration is parallel to the c axis (Fig. 9, c). In the region 6  $\mu$  to 7  $\mu$  there is no trace of a

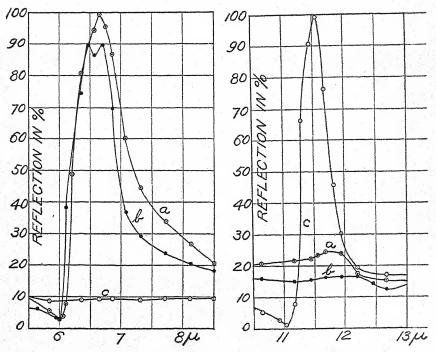


Fig. 10-11. Reflection from aragonite. a, vibrations ||a| axis; b, vibrations ||b| axis; c, vibrations ||c| axis.

band, but in the second region there is a very strong band falling sharply at 11.55  $\mu$ , with a reflecting power of more than 99 per cent. This band like the first band of curve a, must determine the position of maximum absorption. At 14.06  $\mu$  there is a small band which coincides in position and of about the same intensity as the band of the extraordinary ray of calcite. In fact the two curves are very similar except for the shift of the principal band which for calcite falls sharply at 11.30  $\mu$ .

#### SUMMARY.

The results of the foregoing investigation may be summarized as follows:

1. The absorption and reflection curves of calcite and aragonite, as dependent upon the direction of vibration between 1.7  $\mu$  and 15  $\mu$ , show three regions of characteristic bands at 6.6  $\mu$ , 11.5  $\mu$  and 14.1  $\mu$  respectively.

2. For calcite the reflection band in the first region is complex with two principal maxima at 6.46  $\mu$  and 6.96  $\mu$  and a third smaller

maximum at  $6.70 \,\mu$ . For aragonite there are two bands, one simple band with maximum at  $6.65 \,\mu$  and one complex band of two maxima at  $6.46 \,\mu$  and  $6.70 \,\mu$  respectively. In the second region the bands for calcite and aragonite are very similar but shifted in position as follows: calcite 11.30  $\mu$ , aragonite 11.55  $\mu$ . But the bands for the two crystals coincide in the third region.

Calcite - extraordinary ray

14.06  $\mu$ , ordinary ray 14.17  $\mu$ .

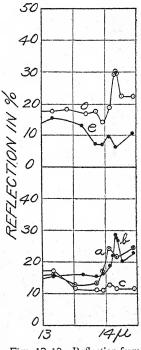
Aragonite — c

14.06  $\mu$ , a and b 14.17  $\mu$ .

- 3. The first bands occur only in the ordinary ray for calcite and the a and b directions for aragonite. For both crystals the second band is present only in the direction of the acute bisectrix. The shifted band at 14.17  $\mu$  occurs only in the obtuse bisectrix for both crystals.
- 4. That with exception of the band at  $2.46 \mu$  absorption characteristics in a biaxial crystal are dependent upon the direction of

vibration and independent of the ray direction through the crystal.

5. At 14.06  $\mu$  the reflection bands for the acute bisectrix in both substances have corresponding absorption bands which are very shallow. In the obtuse bisectrix the absorption band for calcite falls at 14.06  $\mu$  while the corresponding reflection band is shifted to 14.17  $\mu$ .



Figs. 12-13. Reflection from aragonite and calcite.  $\alpha$ , vibrations  $\parallel \alpha$  axis; b, vibrations  $\parallel b$  axis; c, vibrations  $\parallel c$  axis; c, ordinary ray; c, extraordinary ray.

- 6. The characteristic bands may be determined more advantageously by reflection than absorption, first on account of the difficulty in working with sections sufficiently thin for sharp bands, secondly on account of small errors which may result from impurity of the substance. A small per cent. of any impurity of high absorbing power in sections of appreciable thickness, may vitiate the results to a considerable degree. By the method of reflection such an error would be inappreciable.
- 7. From the physical similarity of the anhydrous carbonates of the calcite and aragonite groups, it may be assumed with safety that any characteristic of one of the members will apply equally well to all of the carbonates of that group. Accordingly the characteristic absorption and reflection bands at  $6.6~\mu$  are not present in the acute bisectrix, at 11.5  $\mu$  they occur only in the acute bisectrix, for all of the anhydrous carbonates. The bands at 14  $\mu$  are present in the absorption and reflection curves of each of the principal directions of vibration.

The present investigation has been carried out during the past year under the direction of Professors Nichols and Merritt, whom the author wishes to thank most heartily for the many facilities placed at his disposal and for their never-failing interest in the progress of the work. He is also much indebted to Dr. W. W. Coblentz, of the Bureau of Standards, for advice based upon his extended experience in radiometric work, to Professor Shearer for many useful suggestions, and to Professor Gill, of the Department of Mineralogy, for kindly advice in mineralogical matters, and for his friendly interest shown in other ways.

CORNELL UNIVERSITY, August, 1908.

#### PROCEEDINGS

#### OF THE

## AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FORTY-SIXTH MEETING.

A MEETING of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, February 27, 1909. President Henry Crew presided.

The following papers were presented:

The Radiation from Neutral Electric Systems. Daniel F. Comstock. Thermoelectric Behavior of Tungsten and Tantalum. (By title.) WM. W. Coblentz.

The New Magnetic Charts of the United States for 1905. (Illustrated by lantern slides.) L. A. BAUER.

On the Radioactive Deposits from Actinium. J. C. McLennan.

Determination of the Frequency of Glow-Arc Oscillations. W. G. CADY.

The Number of Free Corpuscles per Unit Volume of the Metals, Gold, Platinum and Silver. B. J. Spence.

Change of Intensity and Rate of Decay of Gas Phosphorescence with Variation of Gas Pressure. C. C. TROWBRIDGE.

The Longitudinal Pressure of Sound Waves. (By title.) Elmer E. Hall.

The Radiation from Gases Heated by Sudden Compression. E. F. NICHOLS and G. B. PEGRAM.

Note on Dispersion Theories. A. TROWBRIDGE.

ERNEST MERRITT,
Secretary.

Note on the Cathode Equilibrium of the Weston Normal Cell.

By F. A. Wolff.

THE paper deals with the value of the Weston cell obtained immediately after it is completed by bringing the mercury into contact with the paste, and furnishes a crucial test of the theory regarding the

equilibrium conditions found in the cell which was recently advanced by Hulett.<sup>1</sup>

According to Hulett, mercurous sulphate is hydrolized by a neutral saturated solution of cadmium sulphate with the formation of a basic mercurous sulphate, and equilibrium is reached when the concentration of the free acid is equal to .08 mol per liter. Since the acid concentration corresponding to saturation of the solution with basic mercurous sulphate was found to be .00045 mol per liter, this would call for the hydrolysis of a considerable quantity of mercurous sulphate and the formation of a corresponding amount of basic mercurous sulphate.

In order to account for the value of the Weston cell set up in the ordinary manner which corresponds to the mercury concentration of a saturated solution of mercurous sulphate in saturated cadmium sulphate, Hulett assumes that the equilibrium condition above referred to is rapidly attained in the cell on account of the hydrolysis being accelerated at the "plain" mercury surface, the products being prevented from leaving the cathode surface by the resistance to diffusion offered by the paste. According to this theory, the value of a Weston cell freshly set up should rapidly increase by approximately z millivolts, the increase observed by Hulett in his rotation cells, while the solution in contact with the mercury cathode is being saturated with basic mercurous sulphate. This value would then begin to decrease to the value ordinarily regarded as normal, on account of the sulphuric acid set free by the continuation of the hydrolysis.

To test this theory a number of cells were constructed in the following manner: Cadmium amalgam was introduced into one limb of an H-type This was covered to a depth of one half centimeter with a saturated cadmium sulphate solution to which finely pulverized crystals of cadmium sulphate were added until no free solution was observed over the crystals. The paste, freshly made up, was next introduced and, after tilting the cell, mercury was poured into the second limb and the cross-arm. The cell was then held in an inclined position for from five to ten minutes in a 25° oil-bath in order to bring the materials to that temperature. Connections to the potentiometer having been completed, observations could be made immediately after bringing the mercury into contact with the paste, thus completing the cell. This method made it possible to obtain a rough instantaneous value from the magnitude of the initial deflection, and actual measurements could be made within ten seconds. havior to be expected on the theory proposed by Hulett was not found, so that it may be safely concluded that the assumption of accelerated hydrolysis at a mercury surface does not apply to the Weston cell as ordinarily set up. Further work suggested by these experiments in contemplated.

<sup>1</sup> Phys. Rev., Vol. 27, p. 337, 1908.

THE NUMBER OF FREE CORPUSCLES PER UNIT VOLUME OF THE METALS GOLD, PLATINUM AND SILVER.<sup>1</sup>

BY B. J. SPENCE.

DRUDE<sup>2</sup> has developed in his work on the optical properties of metals a theory of dispersion, based on the assumption that in the metals there exist two kinds of corpuscles, the conducting and vibrating corpuscles. He arrives at the following equations

$$na = \sum \frac{r_{\lambda} N_1}{c \left(r^2 + \frac{4\pi m^2 c^2}{e^4 \lambda^4}\right)}, \qquad (1)$$

$$n^{2} - a^{2} + 1 = \sum_{\lambda^{2} - \lambda_{0}^{2}} \frac{\theta_{h} N_{h} \lambda^{2}}{\lambda^{2} - \lambda_{0}^{2}} - 4\pi \sum_{\lambda^{2} - \frac{4\pi m^{2} c^{2}}{c^{4} \lambda^{2}}} \frac{N_{1} \frac{m}{c^{2}}}{r_{\lambda}^{2} + \frac{4\pi m^{2} c^{2}}{c^{4} \lambda^{2}}},$$
 (2)

where  $\alpha$  is the absorption coefficient of the metal, n its refractive index, e the charge (3 × ro<sup>-10</sup> C.G.S. electrostatic units), m the mass (.55 × ro<sup>-27</sup> gm.), e the velocity of light in vacuo,  $\theta_k M_k$  is of the dimensions of a dielectric constant,  $\lambda_0$  the wave-length corresponding to an absorption hand in the ultra-violet, and  $r_\lambda$  is defined by  $\sigma_\lambda = N_1/r_\lambda$ , where  $N_1$  is the number of corpuscles per unit volume and  $\sigma_\lambda$  is the conductivity as a function of the wave-length.

The first term of (2) is the contribution due to the vibrating corpuscle, and the remaining terms of the right hand-member of (1) and (2) are the contributions due to the conducting corpuscle.

If we neglect the contribution due to the vibrating corpuscle we obtain two equations in two unknown quantities,  $M_1$  and  $r_{\lambda}$ , which on solution give

$$r_{\lambda} = \frac{4\pi mc}{e^2} \frac{n\alpha}{\lambda(\alpha^2 - n^2 + 1)} = 2.3 \times 10^3 f(\lambda), \tag{3}$$

$$N_{1} = (a^{2} - n^{2} + 1) \frac{mc^{2}}{e^{2}} (4\pi (f(\lambda))^{2} + 1/\lambda^{2})$$

$$= .55 \times 10^{13} (a^{2} - n^{2} + 1) (4\pi (f(\lambda))^{2} + 1/\lambda^{2}).$$
(4)

The absorption coefficients a are known from the work of Rubens and Hagen,<sup>3</sup> and the refractive indices n are known from the work of the writer, which were reported at a previous meeting.<sup>4</sup>

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the New York meeting of the Physical Society, February 27, 1909.

<sup>&</sup>lt;sup>2</sup> Drude's Ann., 14, 936, 1904.

<sup>3</sup> Phil. Mag., 7, 157, 1904.

<sup>4</sup> Washington, D. C., April, 1908.

The value of M for silver, taken as a mean of the values obtained for various wave-lengths where the values were constant is  $.37 \times 10^{23}$ . The values of N for platinum and gold are  $.82 \times 10^{23}$  and  $.33 \times 10^{23}$  respectively. These were also taken as a mean value of several values for various wave-lengths where no constant variation appeared.

THERMOELECTRIC BEHAVIOR OF TUNGSTEN AND TANTALUM.<sup>1</sup>
By WM. W. Coblentz.

LURTHER improvement in the construction of thermopiles must come through the reduction of the heat capacity of the junctions. Tantalum is obtainable in fine wires; it is pliable and does not oxidize readily at ordinary temperatures, and hence, suggests itself as a substitute for iron (steel) in connection with constantan. Observations were made on the thermoelectric power of couples made of copper-tantalum and copper-tungsten, the temperature range being from — 180° to + 300° C. The results show that throughout the range investigated the thermoelectric power of the copper-tantalum is about 4.1 microvolts per degree, which is one tenth that of a copper constantan couples.

The thermal electromotive force curve of tungsten-copper is rather unusual in that its inversion temperature occurs at about 40° C. For temperatures below — 100° C. the thermoelectric power is about 3.8 microvolts per degree while above + 200° C. the thermoelectric power is about 4.5 microvolts per degree. In both couples the direction of the current is the same as that of a copper-constantan couple.

<sup>1</sup>Abstract of a paper presented at the New York meeting of the Physical Society, February 27, 1909.

#### THE

## PHYSICAL REVIEW.

THE EFFECT OF LOW TEMPERATURE ON SOME OF THE PHYSICAL PROPERTIES OF A SERIES OF IRON-CARBON ALLOYS.

By C. W. WAGGONER.

THE series of experiments described below was undertaken with the view of determining how the temperature of liquid air affects the magnetic permeability, the magnetic hysteresis and the expansion coefficient of a series of iron-carbon alloys; and how these properties change with varying chemical composition.

The effect of low temperatures on the magnetic hysteresis, magnetic permeability and electrical conductivity has been studied to some extent before but with alloys of iron of which the chemical composition and definite, previous heat treatment were in many cases unknown.

A very exhaustive study of the effect produced by liquid air temperatures on the mechanical properties of iron and its alloys has been made by R. A. Hadfield.<sup>1</sup>

Thiessen  $^2$  has investigated the hysteresis loss of iron and steel at 100° C., 20° C. and about - 70° C., the latter obtained by using solid CO $_2$ . He found that for soft wrought iron the hysteresis increased with decreasing temperature when the maximum magnetizing field caused magnetic saturation, and that the reverse was true for low magnetizing forces. The same effects of temperature were found for annealed crescent tool steel.

<sup>1</sup> Jour. Iron and Steel Inst., Vol. LXVII., p. 147, 1905.

<sup>&</sup>lt;sup>2</sup> Thiessen, Phys. Rev., Vol. VIII., p. 65.

Fleming and Dewar<sup>1</sup> found that the magnetic permeability of annealed soft Swedish iron decreased when cooled in liquid air for all magnetizing fields, but for the same iron unannealed they found an increase in the permeability at the low temperature. They found also no change in the hysteresis loss of a sample of soft transformer iron, for varying values of the magnetic induction, when cooled in liquid air. T. Claud <sup>2</sup> working with soft iron found a slight tendency to lower hysteresis and permeability at the lower temperature. Honda and Shimizu <sup>3</sup> using Swedish iron, found that cooling in liquid air diminished the magnetization in low fields, but increases it in the strong, the change amounting to about two per cent. They also found that the hysteresis loss was decreased in weak inductions and increased in the strong by cooling in liquid air.

Dr. Fleming 4 in a note to the Iron and Steel Institute, gives some further results on the magnetization of two steels (0.055 per cent. C and 0.29 per cent. C) at the temperature of liquid air. He found that the effect of low temperature on the permeability depended on the previous heat treatment. The low carbon iron, in the annealed state, gave an increase in the permeability for all fields when at the low temperature; while the high carbon steel, annealed, had its permeability decreased when in liquid air. He says: "Broadly speaking, it seems as if the result of low temperature on iron containing a large per cent. of carbon was to decrease the permeability, whilst an opposite effect was produced upon iron containing a small percentage of carbon." J. Stauber working with three steels (no analysis given), found that the lowering of temperature is accompanied by a decrease in the hysteresis loss; but that with higher magetizing fields (30 gauss), both permeability and hysteresis loss increased with decreasing temperature.

The steels used in the following tests were made by Dr. J. A. Mathews, of the Crucible Steel Co., Syracuse, N. Y., to whom the writer wishes to express his gratitude not only for the steels, but also for the complete chemical analysis. These steels were made

<sup>&</sup>lt;sup>1</sup> Fleming and Dewar, Proc. Roy. Soc., Vol. 60, p. 81, 1896.

<sup>&</sup>lt;sup>2</sup> Claud, C. R., Vol. CXXIX., p. 409, 1899.

<sup>&</sup>lt;sup>3</sup> Honda and Shimizu, Jour. Coll. Sc., Tokio Univ., Vol. XX., 1905.

Fleming, Jour. Iron and Steel Inst., Vol. LXVII., p. 237, 1905.

<sup>&</sup>lt;sup>5</sup> Stauber, Le Lumiere Elec., Vol. I., p. 120, 1908.

Chemical Analysis.

Mark.	C	P	Si	Mn	S
P.I.	.058	Trace	.008	.071	-
A1	.60	.013	.15	.14	.012
A2	.74	.012	.16	.14	.013
A3	.89	.010	.19	.155	.013
A4	.98	.012	.16	.15	.013
A5	1.18	.012	.14	.14	.013
A55	1.26	.012	.16	.17	.014
A6	1.37	.011	.19	.16	.012

by the crucible process and after being rolled were allowed to cool in the air. The composition of the different specimens is given in the preceding table.

The low carbon iron, marked P.I. in the analysis was kindly loaned the writer by Professor Bancroft, of the Department of Chemistry, Cornell University. The rods were all 5% inch in diameter and 45 cm. in length. Previous to the magnetic tests the steels were all annealed in a platinum furnace, by heating the whole at 1000° C. for two hours and then allowing them to cool in the furnace. It is assumed that this heat treatment removed the effects of machining the steels. Unfortunately the steel marked A2 was mislaid while the magnetic tests were being made and so it was not included.

The ballistic method was used to measure the magnetic quantities. Taylor has found that a heavily damped galvanometer gives more accurate results in magnetic measurements than one with small damping, because the creeping up of the induction to its final value, for any given field, takes an appreciable time. Stewart used a voltmeter, without its series resistance, as a galvanometer for hysteresis measurements, calibrating it with a standard condenser and known E.M.F. Following this suggestion a galvanometer was made from the parts of a Weston voltmeter. The coil, wound on an aluminum form, was suspended by a fine silk fiber; the current being carried into the coil by two small spiral springs of silver. These springs were so adjusted that the silk fiber fur-

<sup>&</sup>lt;sup>1</sup> Taylor, Phys. Rev., Vol. XXIII., p. 95, 1904.

<sup>&</sup>lt;sup>2</sup> Stewart, Phys. Rev., Vol. XXI., p. 158, 1903.

nished sufficient torsion to just bring the coil to its zero position after it had been given a deflection. The galvanometer was calibrated with a standard condenser and a known E.M.F., and its constant was checked up several times during the test. This form of galvanometer proved to be very satisfactory and readings could be made quite rapidly. In making the readings it was found that in the time necessary to adjust the resistances for the following reading, the galvanometer coil would settle back to its zero and be ready for the next throw.

In order to avoid the cumulative effect of an error in any previous reading of the ballistic throw, the method of operating by steps from one extremity of the cycle, given by Ewing, was used. The upper half of the hysteresis cycle was obtained in this way and the area of the plotted curve measured with a planimeter for the hysteresis loss. With each specimen three cycles were taken, both at room temperature and with the specimen in liquid air, for three values of the magnetic induction. The ballistic coil was wound on the outside of the magnetizing coil and at its center. No attempt was made to correct for the demagnetizing effect of the ends of the rods,

$$\left(\frac{\text{length}}{\text{diameter}} = 75\right)$$
,

and since they all had the same length and approximately the same diameter this correction would not affect the values given when compared among themselves. A small coil was wound on the outside of the magnetization coil and a current passed through it to compensate for the effect of the earth's field in the iron. In making the tests at the low temperature the magnetizing coil and the specimen under test were placed in a long vertical Dewar tube and covered with liquid air. As the air evaporated, more was added so as to keep the coil and specimen completely and continually covered. No attempt was made to measure the temperature change which took place as the air evaporated and new air added, but the tests were never started until the violent ebullition of the air had ceased, indicating that the whole mass had reached the lowest temperature. The high temperature tests were made at

<sup>1</sup> Ewing, Magnetic Induction in Iron, p. 356, 1904 ed.

about 20° C., that of the room. In the case of the low carbon steels, since the hysteresis loss is small, several of the tests were repeated in order to make sure of the values obtained.

An inspection of the data in Table I. shows that for the lowest carbon iron the permeability, when at the temperature of liquid air is slightly higher than its value at room temperature for the highest value of the magnetic induction, and decreases for the lower values. Also, the hysteresis loss for the smallest induction has a smaller value when at the lower temperature, but at higher values of the induction the hysteresis loss is greater at the low than at room temperature. This is in agreement with the work of Honda and Shimizu 1 on a Swedish low carbon iron and Dr. Fleming 2 working with 0.05 per cent. carbon iron. For all the other specimens the effect of low temperature is to decrease the permeability and increase the hysteresis loss for all values of the magnetic induction studied. In order to study the change in the hysteresis loss with varying percentages of carbon, the Steinmetz 1 law  $W = \eta B^{1.6}$ , was used, computing the value of  $\eta$  for the highest induction studied.

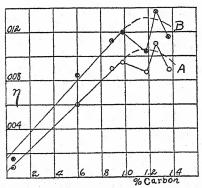


Fig. 1. Showing the relation between the hysteresis coefficient and the carbon content. Curve A represents the relation at 20° C. Curve B represents the relation at -180° C.

The curves given in Fig. 1 show the relation between the hysteresis coefficient and the percentage of carbon. It will be seen that up to .9 per cent. carbon the line has been drawn straight,

<sup>1</sup> Loc. cit.

<sup>2</sup> Loc. cit.

<sup>&</sup>lt;sup>3</sup> Steinmetz, Am. Inst. E. E. Trans., Vol. IX., 1892.

TABLE I.

	ber cent.	68.4	!	1	39.0	1	-	5.3	1	1	26.1	1	1	20.8	-	-	25.2		1	29.5
-	per	.00			8		× '										2			
	f.	00158	١	1	$.0083_{8}$	1	1	.01132	1	1	.01204	١	1	.01045	1	- 1	.01378	1	1	01158
27	Coercive Force Hc.	1.6	1	1	7.0	١	1	10.5	Name and Address of the Address of t	1	11.0	-	1	8.6	]	1	12.6		1	10.5
30° C.	Ħ	335.6	0.869	814.8	288.9	356.2	407.4	247.7	278.9	174.7	239.7	242.1	147.0	257.1	303.4	219.2	209.3	198.2	125.2	241.1
At -180° C.	Hmax	51.1	50.6	10.8	45,9	25.4	10.8	45.0	22.6	11.1	44.0	24.0	11.0	45.7	22.6	11.1	46.0	21.8	11.5	45.0
AND ADDRESS OF THE PARTY OF THE	Bmax	17,110	14,380	8,800	13,260	9,048	4,400	11,150	6,305	1,940	10,550	5,810	1,618	11,750	6,858	2,433	9,630	4,320	1,440	10.850
	М	9,390	5,809	1,500	30,060	20,970	2,690	33,060	12,464	1,283	32,950	12,000	1,282	33,980	12,112	1,706	32,570	9,584	1,186	33 160
	lt.	.00094	-	1	.00603	1	-	.00903	I	- 1	.00955	1	1	.00865	1	1	10110.	1	I	00894
	Coercive Force Hc.	0.75	1	1	5.1	1	l,	8.0	1	1	8.5	1	1	7.5	ı	l	9.3	1	1	8.0
	#	330.3	723.7	880.0	321.7	481.3	470.2	304.7	340.5	207.8	276.9	298.8	175.2	323.5	372.9	258.1	269.7	265.4	165.5	349.5
° C.	Hmax	51.3	19.8	10.0	41.7	18.8	9.4	36.6	18.5	9.1	39.0	20.0	0.6	35.7	18.5	9.6	35.7	16.3	8.7	30.9
At 20° C.	Bmax	16,950	14,330	8,800	13,416	9,048	4,420	11,150	6,300	1,891	10,800	5,976	1,577	11,550	6,900	2,478	9,630	4,326	1,440	10,800
	М	5,470	3,741	1,839	24,250	18,100	4,100	27,000	10,518	1,283	27,120	10,794	1,144	27,360	10,340	1,434	26,040	7,235	1,125	25,410
	Carbon.	.058	2	:	09.	3	3	-89	3	,	86:	3	3	1.18	3	•	1.26	3	:	1.37
	No.	PI	;	:	A1	,,	3	A3	;	*	A4	•	ä	AS	3	3	A55	:	*	3.6

while from that point the dotted portion indicates that the maximum is reached about 1.2 per cent. carbon, and then shows a tendency to decrease. Dillner and Enström 1 have shown that up to .5 per cent. carbon the relation between the hysteresis coefficient and the percentage of carbon is a straight line. A justification for the dotted portion of the curves given in Fig. 1 was found in Dr. Carl Benedicks' 2 classic thesis. Benedicks made a very careful study of the magnetic properties of a series of steels made in an electric furnace. The steel was studied in three states; annealed, forged and tempered.

Fig. 2 shows the curves plotted from Benedicks' data (page 150) on the steels in the annealed and forged state.

In Fig. 2 it will be seen that the curves have a very well defined maximum at about 1.32 per cent. carbon, and that the curve for the

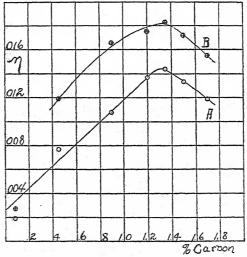


Fig. 2. Showing the relation between the hysteresis coefficient and the carbon content. Plotted from Benedicks' data. Curve A represents the relation for the stee annealed. Curve B represents the relation for the steel forged.

alloys that were forged lies above that for the annealed alloys, showing that the forging had a magnetic hardening effect on the steels.

<sup>&</sup>lt;sup>1</sup> Dillner and Enström, Jour. I. & S. Inst., Vol. LXVIII., p. 408, 1905.

<sup>&</sup>lt;sup>2</sup> Reserches Physiques et physico-chemiques sur l'acier au carbone, Carl Benedicks, Upsala, 1904.

T. Swindon<sup>1</sup> has studied the magnetic properties of a series of carbon tungsten steels containing a constant percentage of tungsten. The writer has taken the liberty to reproduce some of Swindon's curves, showing the relation between the hysteresis loss and the carbon content, since they seem to confirm those of Benedict's and his own.

The curves shown in Fig. 2a are taken from Swindon's paper and they show the effect of heat treatment.

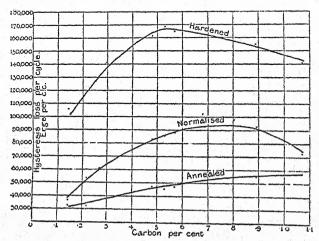


Fig. 2a. Showing the relation between the hysteresis loss and the carbon content. Taken from Swindon's paper. The "Normalizing" treatment consisted in heating to 950° C., holding that temperature for 15 minutes and then allowing the rods to cool freely in the air.

From Fig. 2a it will be seen that the curves, for the steels in the normalized and hardened conditions, resemble those in Fig. 1 and Fig. 2 in this, that the hysteresis loss reaches a decided maximum as the carbon content increases and then decreases. The position of the maximum, in the case of the tungsten steels, depends upon the degree of thermal hardening. The steels in the annealed state seem to approach a maximum at about 1.1 per cent. carbon; the series, however, does not increase sufficiently in carbon content to indicate a decrease from this maximum as the carbon increases.

Benedicks 2 also found the relation between the hysteresis coeffi-

<sup>1</sup> Swindon, The Electrician, Vol. LXII., pp. 830-832, 1909.

<sup>&</sup>lt;sup>2</sup> Loc. cit., p. 153.

cient (at saturation) and the coercive force to be a fixed ratio. So Fig. 3 was plotted from the data at room and liquid air temperatures. The value of the slope for the alloys at room temperature was found to be .00113; while that at liquid air temperature was .00108.

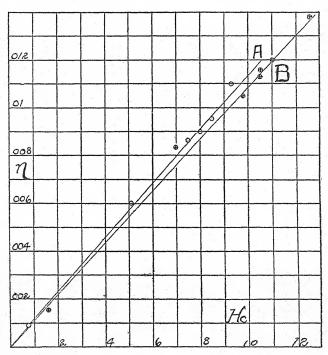


Fig. 3. Showing the relation between the hysteresis coefficient and the coercive force. Curve A represents the relation at 20° C. Curve B represents the relation at — 180° C.

The tests show that the hysteresis loss at liquid air temperatures, for the higher magnetizations, was always increased; so the percentage increase in  $\eta$ , when the steel was at the lower temperature was computed and will be found in the data in the column  $J\eta$  in per cent. The values in the column are plotted against the percentage of carbon and the curve is given in Fig. 4.

It will be seen from the curve given in Fig. 4 that the increase in hysteresis loss for a low carbon alloy is rather large and as the carbon increases this increased loss grows smaller, reaching a minimum value at about 1.1 per cent. carbon, beyond which point it again in-

creases. The resemblance should be noted between the curve (Fig. 4) with its minimum at 1.1 per cent. carbon, and the revised iron-carbon diagram given by Upton 1 with its minimum at 1 per

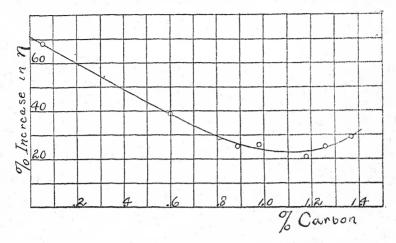


Fig. 4. Curve showing the increase (in per cent.) of the hysteresis coefficient when the steel is at the temperature of liquid air and percentage of carbon.

cent. carbon. Howe <sup>2</sup> finds that the tenacity of an iron-carbon series increases with small percentages of carbon, reaching a maximum at about 1.2 per cent. carbon and then decreasing with increased carbon. Just what bearing the iron-carbon diagram has on the curve given in Fig. 4 the writer is unable to say, for the diagram itself has been the subject of much discussion, and many changes have been proposed.

The increase in the hysteresis coefficient (in per cent.) for the forged steel over the steel in the annealed state was computed from Benedicks' <sup>3</sup> data and plotted in Fig. 5.

The curve given in Fig. 5 bears the same shape as that given in Fig. 4, showing a minimum value of the hysteresis coefficient at about 1.32 per cent. carbon. It should be remarked, also, that the other constituents of Benedicks' alloys, manganese, silicon, sulphur and phosphorus vary rather widely, which makes strict comparison of the two curves impossible. However it is safe to say that the

<sup>&</sup>lt;sup>1</sup>Upton, J. Phys. Chem., Vol. XII., p. 507, 1908.

<sup>&</sup>lt;sup>2</sup> Howe, Iron, Steel and Other Alloys, 1903, p. 162.

<sup>3</sup> Loc. cit.

effect of the low temperature on the magnetic hysteresis of steel is similar to the magnetic hardening produced by forging.

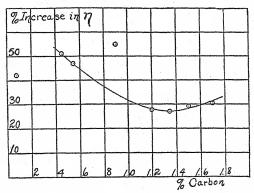


Fig. 5. Showing the carbon content and the increase in hysteresis coefficient from the annealed to forged condition.

#### SUMMARY.

A brief summary of the results is given below.

- 1. The effect of low temperature on an annealed low carbon iron is to increase both permeability and hysteresis loss in high fields, but to decrease both for very low fields.
- 2. For higher carbon steels, annealed, the effect of low temperature is to increase the hysteresis loss and decrease the permeability for all fields.
- 3. The ratio  $\eta/Hc$  as given by Benedicks seems to hold for steels at the temperature of liquid air as well as at room temperature.
- 4. The percentage increase in hysteresis loss for high fields when an annealed steel is cooled to the temperature of liquid air is a function of the carbon content. The change in the hysteresis loss decreases with the addition of carbon reaching a minimum about 1.1 per cent. carbon and then increases.
- 5. The change, in the hysteresis loss of a series of iron carbon alloys, produced by liquid air is analogous to the magnetic hardening of steel by forging.

#### THE COEFFICIENT OF LINEAR EXPANSION.

In order to determine the relation between the carbon content and the density of these steels at the temperature of liquid air, Dr. H. G. Dorsey, of our department, kindly determined the mean coefficient of linear expansion for the steels, from room temperature down to the temperature of liquid air, by an interference method already described. The results are shown in Fig. 6. From the curve it will be seen that the effect of added carbon is to decrease the expansion coefficient; and there is no indication of a change in the curve at I.I per cent. carbon as was found in the magnetic

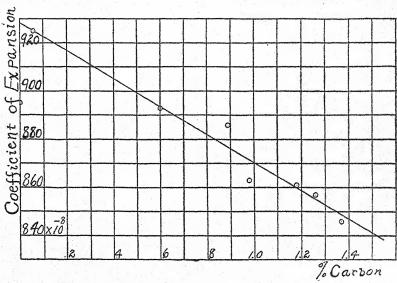


Fig. 6. Showing the relation between the expansion coefficient and carbon content.

tests. Carbonless iron, from the curve, would have a coefficient of expansion of  $928 \times 10^{-8}$ .

The writer hopes to add to the tests above described the specific resistance and the temperature coefficient of resistance of these steels at the temperature of liquid air.

PHYSICAL LABORATORY, CORNELL UNIVERSITY.

Dorsey, Phys. Rev., Vol. 25, p. 88, 1907.

# ON SOME PECULIARITIES OF ELECTRICAL CONDUCTIVITY EXHIBITED BY POWDERS AND A FEW SOLID SUBSTANCES.

By R. H. GODDARD.

THE unilateral conductivity of the mercury arc and the electrolytic cell, the lack of proportionality between E.M.F. and current in the arc and in contact rectifiers, and the change of resistance with time in the case of some heated substances are well-known anomalies of electrical conductivity. The purpose of this paper is to describe some new cases of this sort, which may, perhaps, lead to a new point of attack of the questions of asymmetrical conduction in contact rectifiers, and also of the problem of the coherer.

#### OUTLINE OF THE WORK.

The work herein described grew from a study of the conductivity of loose powders, a subject on which, so far as the writer has been able to learn, practically no work has been done (except in the case of the coherer). In investigations where the specific resistance of salts has been measured, the substances, although existing after purification as powders, have in all cases been submitted to pressures in the neighborhood of 10,000 atmospheres before any measurements of the resistance have been taken.

In the work described in this paper, the writer investigated chiefly three phenomena of conduction through loose powders and certain solid substances: (1) Change of conductivity with time. (2) The development of asymmetry of conduction, that is, difference of conductivity in the direction of and opposite to the current. (3) Deviation from Ohm's law.

#### APPARATUS.

The resistance of the powders examined was very high — e. g., the mean of two values of the specific resistance for powdered cal-

cium sulphide was  $1.72 \times 10^7$  ohms. Thus the conductivity could only be measured by using a thin, wide layer of the powder, a high E.M.F., and a sensitive galvanometer. The apparatus is shown in

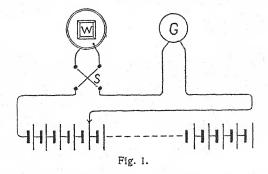


Fig. 1. The powder was sprinkled over a flat copper disk 6 inches in diameter to a depth of about a millimeter. Then a similar disk on which was a lead weight W was placed on this layer. This resistance, or bridge (as a conductor of high resistance will be called, for lack of a better term), was placed in series with a sensitive Broca galvanometer G. An E.M.F. was applied by a battery of forty small storage cells, so that the E.M.F. could be varied by steps of closely two volts from o to 80 volts. A reversing switch S was provided. Throughout the work the galvanometer sensibility was  $7.156 \times 10^{-8}$  amperes per mm. of the scale.

The substances studied were the sulphides of calcium, barium, zinc, and mercury, sulphate of calcium and of mercury, calcium fluoride, barium carbonate, magnesium oxide, mercuric oxide, mercurous oxide, litharge, zinc-dust, mercuric iodide, solid silver iodide, borax, zinc perborate, selenium, and molybdenite.

Of the solid substances used in the experiments, the silver iodide bridge was made by fusing precipitated silver iodide on a glass plate on which had previously been bound two platinum wires, .5 cm. apart, as electrodes. The silver iodide was heated highly so as to reduce some of the silver, to aid in the conduction, and in some cases a trace of silver nitrate was added. This bridge, when cold, had a high resistance, but not so high as to make readable deflections impossible.

Barium sulphide, in the form of hard lumps, was ground down on an emery wheel and finally filed into the form of thin disks.

The mineral molybdenite — the other solid substance examined — was split into thin plates. The other substances call for no special mention

#### CHANGE OF CONDUCTIVITY WITH TIME

It has been observed that when certain solid sulphides, lead sulphide and silver sulphide, are heated by the passage of a current through them, the conductivity increases greatly. On removing the heating current, it is found that the conductivity falls to its original value, then falls somewhat below it, thence slowly increasing to the original value, in about 40 minutes. Other than this, the conductivity of substances—excepting in the electrolytic state—does not change with time.

In the case of the powders and solids here considered, however, the conductivity varied with the length of time the current was applied, at ordinary temperature.

In most cases, when an E.M.F. was applied, the conductivity fell very rapidly at first, then more and more slowly, approaching a limiting value, many times less than the original conductivity. If, after this exposure had continued for some time the circuit was broken, the conductivity slowly regained its original value, the increase being most rapid at first. When the exposure was long enough to make the conductivity constant, the state of the substance seemed fairly steady, that is to say, if the circuit were opened for a short time and then closed, the conductivity soon regained the steady value before the interruption. It was found, in this way, that a momentary breaking or even reversing of the current, did not change appreciably the conductivity of this steady state. Thus it may be assumed that in studying the rise of conductivity after exposure to the steady E.M.F., momentary application of the E.M.F. to get a deflection did not change the conductivity of the substance appreciably.

This change of conductivity with time differed both as regards magnitude and direction with various substances. Of the powders used, calcium sulphide gave the greatest change in magnitude. On one occasion, after an exposure to the E.M.F. of three days, the conductivity rose 60 fold in 21 hours. The initial changes produced in calcium sulphide by the E.M.F. were too rapid to be

<sup>&</sup>lt;sup>1</sup> Streintz, Phys. Zeit., 4, p. 106, 1903.

recorded. A curve is, however, given (Fig. 2, I) showing the effect of application of the E.M.F. to a specimen of calcium sulphide, 40 minutes after a previous, long, application. The first part of the curve shows the effect of the steady application — the second part, the effect after the E.M.F. was removed, it being applied then only long enough to take readings.

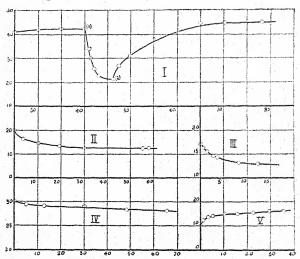


Fig. 2. Time-conductivity change for I, calcium sulphide, current applied during (a-b); II, zinc sulphide; III, magnesium oxide; IV, strontium sulphide; V, solid barium sulphide. Ordinates, deflections, abscissæ, time in minutes.

The substances which exhibited a decrease of conductivity on continued passage of a current were—arranged in the order of magnitude of the effect—calcium sulphide, barium sulphate, borax, zinc sulphide (Fig. 2, II), magnesium oxide (Fig. 2, III), mercurous sulphide, mercuric sulphide, zinc dust, calcium sulphate, solid silver iodide, strontium sulphide (Fig. 2, IV) and litharge.

Those exhibiting an increase were — solid molybdenite, barium carbonate, powdered barium sulphide, solid barium sulphide (Fig. 2, V), and red iodide of mercury.

Barium fluoride, zinc perborate, and selenium, all powdered, showed neither increase nor decrease to any appreciable extent.

#### Effect of a Vacuum.

All the powders that were examined, except selenium, and even the solids, silver iodide and barium sulphide, showed a marked effect when the vessel in which they were contained was exhausted by an air pump. The effect in nearly all cases was the same — a great decrease in conductivity, the change persisting until air had been readmitted, following which there was a gradual rise. With magnesium oxide, the conductivity was reduced to one ninth the initial value by the vacuum, and with other substances the change was comparable with this. The behavior of calcium sulphide is illustrated by Fig. 3, I. For all other substances, except solid barium sulphide, and molybdenite the curves are similar. With barium

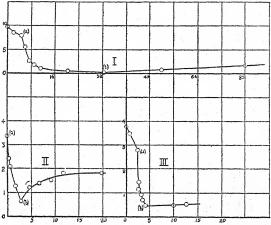


Fig. 3. Effect of a Vacuum on the Conductivity of: I, Calcium sulphide; II, solid barium sulphide; III, powdered barium sulphide. (a) Vacuum produced, (b) air admitted. Ordinates, deflections, abscissæ, time in minutes.

sulphide the rise on admitting air was somewhat abrupt (Fig. 3, II). When the barium sulphide was powdered, the curve obtained resembled that for calclum sulphide (Fig. 3, III) as did also that for the *solid* silver iodide. Solid molybdenite appeared to give a rather sudden fall in conductivity of about 15 per cent. on producing the vacuum, and a corresponding rise on admitting air.

The effect seemed to be more or less independent of the current. With CaS, when the E.M.F. was applied for a short time, at intervals of two minutes after exhaustion, the deflections corresponding to these applications kept growing smaller. After admitting air, they kept increasing. A vacuum now caused them to decrease and a readmission of air caused them to increase.

An E.M.F. was applied steadily to CaS until the deflection had reached a fairly steady value. The E.M.F. was then removed, and a vacuum produced. On reapplication of the E.M.F. the deflection was found to be only 20 per cent. of that just before exhaustion. When the conductivity was at its lowest, under the influence of a vacuum, jarring the bridge caused a rather feeble rise, but after the air had been readmitted and the conductivity had risen, jarring caused a considerable rise.

Later experiments have indicated that the proportionate drop in deflection, after a one-minute application of the vacuum, is the same whether the E.M.F. has been applied for a very short time, immediately before producing the vacuum, or for five minutes.

#### FURTHER OBSERVATIONS.

The powders differed markedly as regards fineness. The calcium sulphide, barium fluoride, magnesium oxide, and the carbonates and sulphates were all very fine. The zinc sulphide was somewhat coarse, while the selenium was the coarsest of all. The other powders were nearly, if not quite, as fine as those first mentioned. The resistances of the powders differed widely, but the copper disks could be used for all powders except zinc dust, which had to be used in a glass tube resembling a coherer.

No polarization, or back E.M.F., could be observed at any time If the bridge—or system containing the powder—were short circuited across the galvanometer, no swing followed. Only when the resistance of the powder was so extremely high that readings could not well be taken could a deflection be observed—the bridge then acting as a condenser.

In the experiments described, copper electrodes were used, but no apparent change was produced when the electrodes were tin, zinc or platinum.

The powdered sulphides gradually produced a thin, bluish film of sulphide on the copper electrodes. This did not influence the results, as a bridge, allowed to stand for three days after having been freshly prepared, showed the same phenomena as a bridge tried immediately after being made.

It was found that after the conductivity of the calcium sulphide had fallen to a fairly steady value, under the influence of an E.M.F.,

the disks with the powder between them could be disturbed in certain ways without changing much the value of the conductivity at that time. When the current was removed for a moment and was then applied again, the conductivity was found to have risen, but it soon fell back to the steady value. If the upper copper disk were now lifted off very carefully, and then replaced, the conductivity was likewise found to have risen, but it soon fell back to the steady value. If, however, the powder itself were stirred or jarred, the conductivity, after the disturbance, was found to have risen much higher — the bridge behaving as if freshly prepared.

The action of a powder, as regards the time-conductivity change, is not always the same. In many trials at different times, calcium sulphide and borax showed a decrease of conductivity with time. Once, however, for each powder, there was an exception, for no apparent reason. The rise with time in the case of calcium sulphide was almost linear, the curve being slightly convex toward the time-axis, while the curve for the borax resembled the hysteresis curve for iron, being S-shaped. These cases could not be repeated.

A peculiar time-conductivity effect was noticed with barium sulphide, which might be called a spontaneous rise of conductivity. It was found that when the barium sulphide was freshly powdered, the conductivity rose to three times its initial value in 3.5 minutes, the E.M.F. being applied only long enough to take readings. investigate this further, a sample of freshly powdered barium sulphide was divided into two parts; one was placed in a vacuum desiccator for twenty hours, and the other exposed to the air of the room for the same time. The conductivity of the former part was found to rise slowly after removal from the desiccator, increasing by one third in twenty minutes, while that of the latter decreased to about one half in two minutes - in each case the E.M.F. being applied only long enough to take readings. When the E.M.F. was applied steadily, the conductivity fell in both cases. To find whether or not the applications of the E.M.F. for a short time were important, a third experiment was performed. Two bridges, as nearly equal as possible, were made from freshly powdered barium sulphide. The conductivity of one, I., was observed immediately after setting up—the other, II., not until five minutes later. After this the conductivity of both was observed at the same time for five-minute intervals for an hour. Bridge I. gave a somewhat greater conductivity at first, but both gave decreasing values (Fig. 4). After the experiment represented by Fig. 4 was performed, the

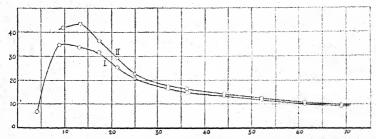


Fig. 4. Spontaneous Rise in Conductivity, freshly powdered Barium Sulphide. I, Bridge no. 1, ordinates, deflections; II, Bridge no. 2, abscisse, time in minutes.

powder was stirred, and the experiment was repeated. This time, the conductivity also rose, but to a much less extent. A later experiment has indicated that the conductivity may increase and remain large if the E.M.F. is not applied often.

A nickel-silver coherer of the ordinary type was examined under various conditions to detect, if possible, a time-conductivity effect, but the results were not consistent. At times, however, the application of an E.M.F. caused a sudden decrease of conductivity, while its removal caused a gradual rise.

#### ASYMMETRIC CONDUCTION.

Certain cases in which conductivity in the direction in which the current is flowing is different from that in the reverse direction are common. Examples of these are the battery, in which a back E.M.F. exists, and the mercury vapor lamp, where a stream of charged particles tends to carry the current in one direction. There are also cases of contact between substances — usually point contact — where the same peculiarity of conductivity exists. It has been shown that, while contacts of silicon and steel, carbon and steel, and aluminium and tellurium act as alternating-current rectifiers, they also exhibit unilateral conductivity with direct cur-

<sup>&</sup>lt;sup>1</sup> Austin, Bull. Bur. Standards, 5, 1, p. 133, 1908.

rent. With the aluminium-tellurium contact, the effect with direct current may be observed even if a no. 20 aluminium wire is melted into a block of tellurium.

It is not necessary, however, that the contact should be that of different substances. It has been found that if a coherer formed by two copper wires touching each other is made to cohere in the ordinary manner, by a spark some distance away, the wires, if separated and held apart a few moments, will not recohere when placed together again, but will do so if the current be reversed. The wires may be again separated and the action repeated several times.

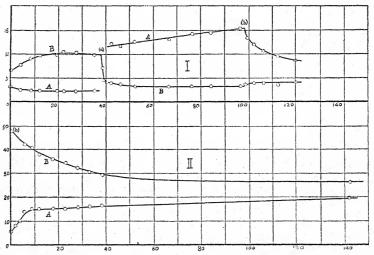


Fig. 5. I, Asymmetric Behavior of Calcium Sulphide; II, Recovery of Calcium Sulphide after I hr. 22 min. exposure to the E.M.F. (a) Current reversed, (b) circuit opened. Ordinates, deflections, abscissæ, time in minutes.

The effects to be described resemble those just considered. It will be convenient to call A the conductivity in the direction of the initial current, and B the conductivity in the opposite direction.

The relation between A and B for calcium sulphide is shown by Fig. 5. The current was kept constantly in the direction A, and brief reversals for B were made at intervals of two minutes, only long enough to take a reading. The current was then reversed, and it will be noticed that here A rose steadily while B fell. This illustrates the steady increase of conductivity in the direction opposite to that in which the current is flowing, characteristic of calcium

sulphide. On opening the circuit, and taking readings for the conductivity at intervals of two minutes—applying the current for as short a time as possible—A fell, while B kept rather constant. It is to be noted that the deflection for A reached a steady value quickly. For B, however, the initial throws grew larger and larger, falling rather rapidly to the same scale division each time. The resistance, then, *increased* in one direction, on opening the circuit. The specimen of powdered calcium sulphide used in this experiment had been previously subjected to reversals.

Two fresh bridges of calcium sulphide were then prepared. One was exposed to the E.M.F. for 18 minutes. When the circuit was opened, A fell slightly, then rose, while B rose, as it had been doing before the E.M.F. was removed. The other bridge was

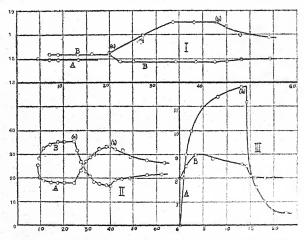


Fig. 6. Asymmetric conduction in: I, Selenium; II, solid silver iodide; III, molybdenite. (a) Current reversed, (b) circuit opened. Ordinates, deflections, abscissae, time in minutes.

exposed to the E.M.F. for I hour 22 minutes. Here the increase in resistance on opening the circuit was clearly marked (Fig. 5, //).

The behavior of coarsely powdered selenium was peculiar. At first the difference between A and B was not marked (Fig. 6, I), but on reversal of the current the conductivity in the direction of the current then flowing fell slightly, while that in the opposite direction rose considerably. The effect on opening the circuit was similar to that of calcium sulphide after a long exposure to the

E.M.F. The conductivities, on reversing, appeared to reach a steady state after a short time. For example, in one case the initial deflections were A, 15; B, 16.8; an E.M.F. was applied, for 88 hours, after which they were, A, 14.5; B, 15, rising quickly to 22. After several reversals a steady state was obtained with A, 15; B, 22.

The bridge of solid silver-iodide described above, showed the asymmetry markedly. The current fell in the initial direction and rose in the opposite direction. This was true on reversal, Fig. 6, II. It should be noticed that with this substance the curves for A and B are of the same shape, one of them being inverted. With this substance, when a vacuum was produced, A dropped to one fourth its value, while B dropped to two fifths its value before the production of the vacuum.

The mineral molybdenite behaved differently from the other substances examined, in that A increased with the time, while B fell. After applying the E.M.F., the conductivities soon reached a steady state. The phenomenon was here complicated by the fact that a given state in the molybdenite tended to persist. In other words, with a perfectly fresh specimen, the E.M.F. produced a state which persisted for a considerable time - the conductivity for this initial direction being permanently above that in the reverse direction. The effects of subsequent reversals were superposed upon this permanent effect. The molybdenite showed the effect clearly after standing for a day. It could be removed from between the copper plates or electrodes, turned over and replaced, and would show the same effect if the conductivity were measured with a current in the same direction through the specimen as before. The state could be obliterated, however, if the specimen were split into laminæ, and some of these were reversed. This state was, curiously, influenced by sparks from an induction coil, several feet away from the apparatus. After a spark had passed, the state was often reversed, and the conductivity, in general, was higher. Such sparks had no apparent influence on the other substances examined. Fig. 6, III, shows the changes in conductivity of a specimen of molybdenite, with a permanent state, after standing over night. It will be noticed that B tended to be permanently above A. In this experiment A and B were in the same direction for a short time after applying the E.M.F.

Asymmetry was found with a coherer of the ordinary form, made of nickel-silver filings. A state of asymmetry would appear more or less suddenly, remain rather constant, and persist even if reversals were made rapidly. The tendency seemed to be for A to remain steady and for B to rise, and B could stay permanently twice A.

When reversals were made, in studying asymmetry, a certain sluggish action was noticed with selenium which was not shown with the other substances. When the current was flowing in the direction A, in selenium, and a steady deflection had been reached, for both A and B, a reversal gave immediately the larger deflection for B, but a reversal back to the original direction did not give the original deflection at once, but the deflection fell rather slowly from the higher.

DEVIATION FROM OHM'S LAW.

The substances that were studied did not show a proportionality of current to E.M.F. In other words, the conductivity depended upon the applied E.M.F.

As has been said, after the E.M.F. had been applied long enough to bring the conductivity to a constant value, it could be removed for a moment, and when reapplied the same conductivity would be shown. It was found that, if the E.M.F. were removed, and various other E.M.F.'s applied in rather rapid succession, readings could be taken of the deflections corresponding to these other E.M.F.'s, which would be perfectly definite and not depend upon the order in which they were applied, and that after this had been done, the original E.M.F. produced closely the original deflection. Hence, at any particular time, agreement with Ohm's law could be tested.

A calibration curve was first made for the galvanometer by applying equal steps of voltage from across a slide-wire in series with a high resistance. The curve in which these increments were plotted against the corresponding deflections was a straight line.

All the powders and the three solids examined showed deviation from Ohm's law, except powered zinc perborate. Arranged in the order of magnitude of the effect; i. e., the magnitude of the curva-

ture, they were, molybdenite (Fig. 7, I), calcium sulphide, solid barium sulphide (Fig. 7, IV), powdered barium sulphide, mercuric

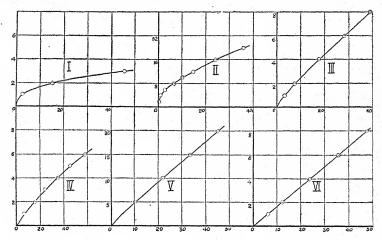


Fig. 7. Deviation from Ohm's Law of: *I*, Solid molybdenite; *II*, solid barium sulphide; *III*, magnesium oxide; *IV*, strontium sulphide; *V*, solid silver iodide; *VI*, zinc perborate. Ordinates, potential by storage cells, abscissæ, deflection.

oxide, zinc dust, magnesium oxide (Fig. 7, III), borax, strontium sulphide (Fig. 7, IV), mercuric iodide, barium carbonate, barium sulphate, barium fluoride, zinc sulphide, solid silver iodide (Fig. 7, V), calcium sulphate, litharge, mercurous oxide, and zinc perborate (Fig. 7, VI), which last gave no sensible deviation whatever. From the curves it is seen that those substances which deviate but slightly do so most strongly at low voltages. In these curves, the ordinates represent the number of storage cells used in obtaining the E.M.F.

The deviation from Ohm's law was present under all conditions except when great pressure was applied. A heavy press used for making pellets for a bomb calorimeter was used to furnish the pressure on a specimen of powdered calcium sulphide. As the pressure was increased, the curves approached a straight line. Figs. 8, *I, II* and *III* show the relation between current and E.M.F. before applying pressure, with considerable pressure, and with the greatest possible pressure, respectively. It will be noticed that Fig. 8, *II*, resembles the curve for selenium.

Even in a vacuum, the deviation from Ohm's law was present.

The marked change in conductivity necessarily caused a change in the curvature, as is evident from Figs. 9, I, III.

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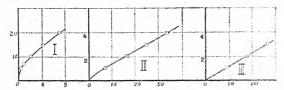


Fig. 8. Effect of Pressure on the Deviation from Ohm's Law in Calcium Sulphide: I, Before applying pressure; II, with considerable pressure; III, with great pressure. Ordinates, potential, by storage cells, abscissæ, deflection.

The deviation did not disappear with current densities many times greater than those ordinarily used in the experiments. When the current density, as indicated by the shunted galvanometer, was increased to 300 times the usual value with calcium sulphide, requiring the application of 40 volts, Ohm's law was not obeyed. When, however, 60 or 80 volts were applied, the current became much larger, and very irregular.

No difference in the effect could be detected after the calcium sulphide had been placed on a glass plate in a closed vessel over water for a day, or in a vacuum desiccator over sulphuric acid.

An electric discharge had a marked defect on the conductivity of zinc-dust, but did not change the deviation from Ohm's law to any

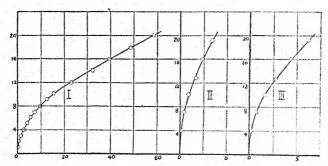


Fig. 9. Effect of a Vacuum on the Deviation from Ohm's Law in Calcium Sulphide: I, Before the vacuum; II, during the vacuum; III, immediately after the vacuum. Ordinates, potential, by storage cells, abscissæ, deflection.

appreciable extent. As the conductivity of zinc-dust was better than that of the other powders used, it was possible to make a bridge of it in the form of a tube coherer. The tube of the coherer was placed one inch from the spark gap of a small induction coil, parallel to the axis of the gap. It was found that sparks caused the conductivity of the zinc dust to increase about 100 fold, but, when steady readings were possible, the deviation was still present. After the sparking, the conductivity of the zinc-dust coherer fell, whether the current were on or off.

A peculiarity of the deviation is that, with the same substance, the upper part of the  $E\!-\!I$  curve is more or less straight. Here, again, there seems to be a general tendency, which is followed except in a very few cases.

The above phenomena, in general, may reasonably be considered as contact phenomena; *i. e.*, changes taking place at the junctures between particles. It is evidently so for powders, and is more or less so in the case of solid silver iodide, barium sulphide, and molybdenite, if it be assumed that, in the first two bodies, there is point contact between the interlocking crystals, and, in the last, line contact between thin laminæ.

This being so, there should be some resemblance between the behavior of powders, and of the coherer. Such a resemblance can be seen by a consideration of what has been already found concerning coherer phenomena.

# THE CONDUCTIVITY OF THE COHERER.

### (a) Particle-coherers.

It has been found that a film of some sort is necessary between the coherer particles. For example, silver filings cannot be used as a coherer, but can be, after exposure to hydrogen sulphide. If exposed too long, however, the efficiency falls off, the film becoming too thick.

Sparks usually pass between the particles. Minute sparks have been observed microscopically even with particles surrounded by Canada balsam.<sup>2</sup> They have also been observed, between steel, across a gap of 0.006 mm., before a galvanometer indicated a cur-

<sup>&</sup>lt;sup>1</sup> A. Blondel, Écl. Élect., 16, p. 316, 1898.

<sup>&</sup>lt;sup>2</sup> L. Arons, Ann. Phys. Chem., 63, 3, p. 567, 1898.

rent. Small particles were observed to fly across before a bridge formed.1

Fusions take place at the contacts. This has been shown by producing coherence in a coherer of iron filings and subsequently removing the loose filings with a magnet, leaving the chains of particles; <sup>2</sup> also, by producing coherence in a tube of brass filings, and observing that the resistance lengthwise of the tube was very much lower than that transversely.<sup>3</sup>

As the pressure of particle on particle is increased, up to the pressure at which the particles come into actual metallic contact with each other, the coherer becomes more and more sensitive.

Lowering the temperature of the coherer produces no result; raising the temperature produces decoherence.

The particles of a coherer may produce effects by being in motion. Brass turnings between two highly charged plates, in oil, may execute an "electric dance," carrying charges to and fro until the turnings finally become welded together as chains.<sup>5</sup> Besides this action, charges on adjacent particles must exert forces tending to draw the particles together. This has been given 6 as an explanation of the deviation of the coherer from Ohm's law. When a coherer is regularly tapped many times a second to produce decoherence, definite deflections of a galvanometer may be had when various E.M.F.'s are applied. The curve giving the relation between E and I is not, however, a straight line, but is concave toward the axis of I, becoming approximately linear with increase of There is apparently no critical voltage. Eccles explained this on the supposition that the particles are free to move, are not circular, and hence are acted upon by a couple, which tends to pull the long axis in line with the current. The E-I curve showed initial curvature in all cases, the curvature persisting for the higher values of E with non-sensitive coherers. (It is to be noted here that in the work described in the present paper all the powders and solids

<sup>&</sup>lt;sup>1</sup> J. Härden, Electrotech. Zeit., 21, p. 272, 1900.

<sup>&</sup>lt;sup>2</sup> T. Sundorph, Wied. Ann. 68, 3, p. 594, 1899.

<sup>&</sup>lt;sup>3</sup> F. Campanille and G. di Ciommo, Elect. Rev., IV., V., 36, p. 353, 1900.

<sup>&</sup>lt;sup>4</sup> P. Jegou, Écl. Élect., 51, p. 82, 1907.

<sup>&</sup>lt;sup>5</sup> R. Malagoli, N. Cimento, 10, p. 279, 1899.

<sup>6</sup> Eccles, Electrician, 47, p. 682, p. 715, 1901.

examined except molybdenite were insensitive to Hertz waves.) The straight part of the curve, then, is reached when most of the particles have turned with their long axes in the direction of the current. This theory, however, seems somewhat disproved by the fact that the same curves have been obtained with nickel filings in kerosene <sup>1</sup> where the resistance to turning ought to be much greater.

# (b) Ball-coherers.

Where the contact is between particles of considerable size, fusion takes place on coherence, as has been shown 2 by the fact that, when two copper wires cohere, it requires a small but measurable pull to separate them.

The conductivity of the ball-coherer has been carefully studied,<sup>3</sup> by means of a coherer, one of the balls of which was held by a spring and could be given a fine adjustment with a screw. Sparking and the attending complications was avoided. When both contacts were heated, the resistance of the coherer decreased, regaining the initial value on cooling. When one contact only was heated, the resistance was different in the two directions—the potential difference of the coherer being lower when the electricity flowed from the hotter to the colder side. For a considerable range, the resistance did not depend on the pressure between the balls.

The deviation from Ohm's law was peculiar. As the E.M.F. was slowly increased, the current increased, at first slowly, and then more and more rapidly, the E.M.F. approaching a constant value, the critical voltage, which was characteristic of each metal. Guthe and Trowbridge explained this by considering that as the E.M.F. becomes greater, the tension across the film at the contact increases, and ions break through and conduct. The more filled up this area of film is, the less readily the ions go over, thus creating a tendency for the area of contact to become greater and greater and the potential difference to become less and less with increasing current until the critical voltage is reached. As the potential does not vary through a considerable range of current, we cannot have to do with a time rate of heaping up of ions. It is a curious fact that the

<sup>&</sup>lt;sup>1</sup> Huth, Phys. Zeit., 4, p. 594, 1903.

<sup>&</sup>lt;sup>2</sup> Shaw and Garret, loc. cit., p. 413.

<sup>&</sup>lt;sup>3</sup> Guthe and Trowbridge, Phys. Rev., 11, p. 22; 12, p. 245.

product of the critical voltage and the atomic weight is approximately a constant.

Guthe and Trowbridge explained negative action, or the increase of resistance of a coherer under increasing excitation, by considering that, when this action takes place, a small particle is lodged between two larger ones, from which position it is displaced — thus increasing the resistance — when the potential difference between the larger particles is increased.

This was found experimentally to be so. Such negative action takes place with powdered lead dioxide and some of the soft metals. With feeble waves there is coherence, but with powerful waves there is a relapse to the state of high resistance. A former explanation of this was that the feeble waves produce bridges which are broken down by the powerful waves.

Asymmetry has been shown by Shaw and Garret 1 to exist for a coherer of two copper wires. It was suggested by the authors, that, as the current density at the points of contact is enormous, an orientation of the particles forming the bridge takes place, "the particles being turned in such a way that they give maximum conduction."

ATTEMPT AT EXPLANATION OF THE CONDUCTIVITY OF POWDERS.

From a consideration of what has been found for coherers, an attempt may now be made to explain the conductivity of powders and of such solids as were examined. The fall, or rise, of conductivity with time had best be considered in detail along with asymmetry.

It seems improbable that the change of conductivity with time is due to a decohering action such as breaking of the chains of particles by heating produced at the junctions. Cooling a coherer produces no change, warming produces expansion and fracture of the junctions, hence decoherence. An experiment was performed to test this point with calcium sulphide. After a steady state of conductivity had been reached, the bridge was cooled to the temperature of ice. No change took place. After the ice was removed the conductivity rose during the warming. This suggests a like action in

<sup>1</sup> Shaw and Garret, loc. cit., p. 413.

the two cases as a jarring produces a decrease of conductivity with the coherer, and an increase with calcium sulphide. Hence the time-conductivity effects would not seem to be due to a rearrangement of particles.

Irregularities might be expected with powders, as with the coherer, "negative action," for example. The occasionally capricious action as regards the time-conductivity effect in powders ought not, then, to appear remarkable.

Because the deviation from Ohm's law is always in the same direction, it must be due to some condition which holds for all powders. It may be explained most easily by supposing that, as the E.M.F. increases, particles that were loose now take part in the conduction either by movements, or by forming temporary chains of particles. The phenomenon may, however, not be so simple.

Since the study of a coherer shows that a surface film is necessary, it seems safe to assume that, with all substances which show change of conductivity with time or deviation from Ohm's law, a surface film is also necessary.

The spontaneous rise is difficult to understand unless it has to do with ionization on fresh surfaces that may be acted upon by the air, as suggested by the following consideration of asymmetry.

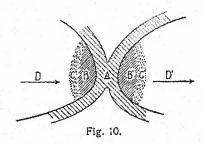
#### ASYMMETRY.

The phenomena connected with the asymmetric conduction of powders are very complex, and it is difficult to give any satisfactory explanation of them. Yet it is desirable to make some attempt at an explanation, however crude it may be. A theory which has been suggested to the writer by some of the views already advanced, has helped him to form some idea of what may take place in a powder that conducts asymmetrically. This theory may not be correct, and, even if it is found to be so, it will probably have to be modified greatly.

Asymmetric conduction for powders and the coherer may be explained by considering conduction to take place by means of ions in motion. Suppose in Fig. 10, which represents a contact between particles, greatly magnified, A to be the part of the film between the particles. This film is necessary in order to have coherence

phenomena, as there must be something which separates the particles, prevents fusion, and hence causes currents of great density at the points of contact. Suppose B and B' to be the respective parts of the two particles that are most highly heated, C and C' to be regions where the heating is less intense.

It will be necessary to make certain assumptions.



- (a) Owing to the high temperatures at contacts between particles, due to great current density, there should be marked changes of the resistance to motion of electrons, or negative ions, which move across the contact. Hence assume the resistance to motion of the ions in the more heated regions, B and B', to be greater or less than in C and C', depending on the material of the particles.
- (b) Also assume that the film A, though it may have considerable resistance, has small resistance, as a rule, compared with B and B'.

This will help to explain asymmetrical conduction in which the conductivity in the direction of the current decreases with time, while that in the opposite direction steadily increases. If the hotter parts B, B' impede the negative ions more, then, if the current flows from D to D', the ions produced in C will move slower as they approach B. Thus there will first be considerable movement of the ions until there is a kind of opposing assemblage in B. Ions will still pass through and beyond B, but at B' they will be neutralized by positive charges there, as B and B' are charged oppositely, and will not pass to any extent into B' and C'.

If now the current be reversed, the ions will move back at a higher rate, since they are all now moving in the direction of decreasing resistance, and this increased rate means a high initial current. Such a state of asymmetry is found with calcium sulphide and solid silver iodide.

On the other hand, if the regions B, B', and A offer less resistance to the motion than C and C', which are cooler, then, when a current is sent from D to D', ions from C will cross B to B', where they will be neutralized as before. In this case they pass through a region in which they move constantly faster, i. e., the current increases. A steady state is reached when the velocity at any point in the course remains the same.

If the current be now reversed, the condition will differ from that which initially held, in that the ions in B will all be moving in the direction of increasing resistance, and hence the current, depending on the rate of motion, will be small. It will increase, however, if time is given for the ions in C' to pass into B'. This is the case of molybdenite.

It is to be observed that this explanation of asymmetry takes care of the question of the change of conductivity with time.

Since, when the powder is in a vacuum the asymmetry is still preserved nearly unchanged, the vacuum must modify the film A, which is, perhaps, a kind of arc, possibly removing ions, and—to account for the slow rise of conductivity (see curve) — making subsequent passage of ions in A difficult, after this removal.

This theory of asymmetry receives support from certain experimental facts. It has been shown by Streintz 1 that solid silver sulphide when raised from — 200° to 220° falls in resistance from a very high value to 0.1 ohm. At the higher temperature a current of 1 or 2 amperes can be sent through a specimen for several hours without evidence of decomposition. There develops with time, however, an increasing resistance to the flow of the current, without any signs of electrolytic polarization being manifest. This may be due to a gathering of the ions in the poorly conducting substance, which opposes the current even though no polarization exists. The fact that the rate of decrease of resistance with temperature for mercury and lead sulphides is about one fourth that for silver sulphide suggests that the positive atom has something to do with the opposition to motion.

In the aluminium-tellurium rectifier already mentioned 2 it was

<sup>1</sup> Streintz, loc. cit., p. 407.

<sup>&</sup>lt;sup>2</sup> Austin, loc. cit., p. 412.

observed that, when increasing alternating voltages are applied, the rectified current is first in the direction of the thermoelectric current due simply to heating the contact; then, with increasing voltage, the current becomes reversed. The contact here is not extremely small, and the results suggest that a certain amount of heating is necessary before the asymmetric condition becomes established.

It has been shown, that, with a ball-coherer, the potential difference across the coherer does not depend upon the pressure between the balls of which the coherer is made (within certain limits). In this case, the region A, Fig. 10, must be varied, and hence, as was assumed, the resistance must be smaller than that of B or B'.

There are, however, certain weak places in the theory. When the circuit is broken, the heated contacts should cool very rapidly, and the resistance should return promptly to its initial value. To account for the facts, it must be assumed, then, that the ions can diffuse, more and more slowly, in the solid substance of the cold particles, as the asymmetric condition changes for some time after opening the circuit—thereafter remaining constant for hours. The diffusion would, of course, be in such a direction as to equalize the distribution of the ions.

It is difficult to account for the recoherence of two copper wires, unless there is initially a semi-solid film on the surface of the copper, and ions become more or less permanently entrapped in this film — which, in part, constitutes B and B' in the figure — and only slowly diffuse therefrom.

Guthe and Trowbridge¹ in explaining the critical voltage of the ball-coherer considered that, as the current is increased, the area of contact remains constant until the current rises to such a value that a certain maximum number of ions cross the area. If the current be increased beyond this value, the effective area is increased by ions filling up the space exterior to the original area. The theory of asymmetry, then, explains critical voltage of the ball-coherer if it is considered that the region A spreads out on sufficient increase of current.

With balls of different metals, the critical voltage is independent of the direction of the current, but may be less or greater than the

<sup>1</sup> Guthe and Trowbridge, loc. cit., p. 421.

critical voltage of either. This is difficult to explain unless it is supposed that the atoms of the two metals cross the film and combine, during the transit, to form a single ion.

#### SUMMARY.

(a) In general, when an E.M.F. was applied to a powder, or to the solids AgI, BaS, and molybdenite, the conductivity fell, rapidly at first, finally approaching a limiting value. If, after the exposure to the E.M.F., the circuit were broken, the conductivity tended to regain its original value, rapidly at first, then more and more slowly.

In some cases, e. g., with molybdenite, the conductivity rose on application of the E.M.F. In other, still fewer, cases, e. g., with BaF, the conductivity remained constant.

These changes were occasionally (but rarely) reversed in an unaccountable way.

With powdered BaS, the conductivity rose, apparently spontaneously after the substance was powdered.

- (b) While the changes under (a) were taking place, the conductivity was found to be changing in the direction opposite to that in which the current originally flowed, the rates of change of conductivity in the two directions being, in general, opposite at any time; but only in the case of solid AgI were they of the same magnitude. Solid molybdenite alone gave a large permanent difference of conductivity.
- (c) With all the substances examined, except powderd zinc perborate, the current did not increase in proportion to the E.M.F.; i. e., Ohm's law was not obeyed. The E-I curve was always concave toward the I-axis, becoming linear in some cases, for the higher E.M.F.'s. This latter type of curve has already been found to hold for the coherer.

The deviation from Ohm's law was present in all circumstances except under the application of great pressure.

(d) The effect of a vacuum was much the same for all substances examined. When the vacuum was produced, the conductivity fell considerably; rapidly at first, and then slowly. This fall took place with or without the current flowing, and whether the E.M.F. had been applied for a long or a short time, preceding the vacuum.

After the admission of air, the conductivity rose, in general, slowly and at a constant rate.

(e) All these effects were independent of the particular metal between which the substances were placed. Stirring or jarring a powder brought it more or less closely to the condition that held before the E.M.F. had been applied.

Finally a theory depending on slow diffusion of ions in heated contacts between particles is offered in explanation of the above facts.

Worcester Polytechnic Institute, Worcester, Mass., March 15, 1909. No. 6.7

# THE EFFECT OF TORSION ON THERMAL AND ELECTRICAL CONDUCTIVITY.

BY NEWLAND F. SMITH.

VERY few measurements seem to have been made to show the effect of torsion upon the conductivity of metals. In 1899 C. de Szily investigated the variation in the electrical resistance of a constantin wire 350 cm. in length when twisted through angles varying from 0 to  $50\pi$ . He showed that the resistance was increased by torsion, the increase being more rapid than the angle of twist. The maximum increase in resistance amounted to about 4 parts in 10,000. No statement is made regarding the diameter of the wire. So far as the writer knows, no results have been published bearing upon the corresponding thermal problem.

In a recent paper<sup>2</sup> the writer has described a series of experiments to determine the changes produced by tension in the thermal and electrical conductivities of metal bars. The present paper deals with the corresponding effects produced by subjecting the bars to a twisting couple. The experimental method was in all respects the same as in the previous investigation and need not again be described in detail. The apparatus of the previous experiments required only slight modification to adapt it to its present purpose. The lever, by which tension was applied, was removed, and in its place was mounted a cast iron pulley 12 inches in diameter carrying a divided circle by means of which to measure the angle of twist. This pulley at its center engaged the friction clutch attached to the outer end of the bar to be twisted, while the clutch at the other end of the bar was kept from turning by clamping between suitable iron plates. Weights attached to flexible wires wrapped around the pulley produced the twisting couple.

Proceeding as in the earlier experiments, the rod to be twisted

<sup>&</sup>lt;sup>1</sup>C. de Szily, C. R., 128, p. 927, 1899.

<sup>&</sup>lt;sup>2</sup> Phys. Rev., Vol. XXVIII., No. 2, p. 107.

and another rod of the same size and material were mounted side by side having one end of each clamped between heavy pieces of

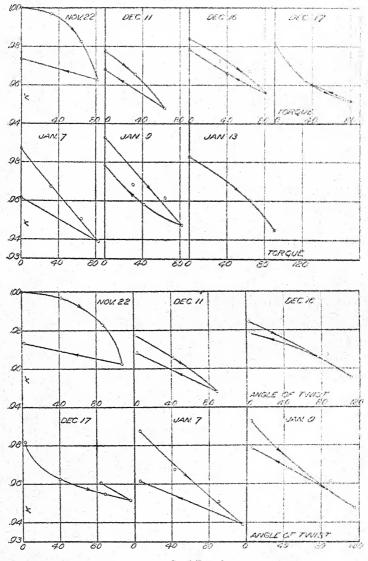


Fig. 1. Steel Bar, B19.

copper which were maintained at a constant high temperature. By means of thermoelectric couples two points of equal temperature

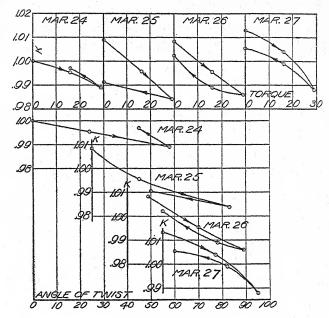


Fig. 2. Iron Bar,  $B_{11}$ .

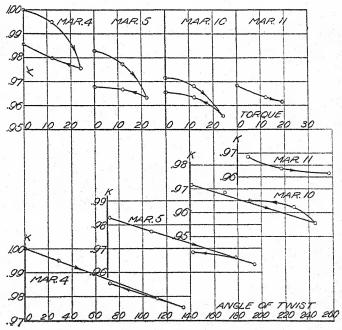


Fig. 3. Copper Bar,  $B_{14}$ .

were located on the two bars about 50 cm. from the copper clamp. The one bar was then twisted while the condition of the other remained unchanged. When the steady state was again reached a new point was found on the twisted bar whose temperature was the same as that of the point previously located on the other bar.

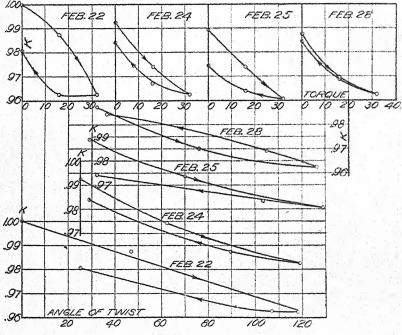


Fig. 4. Brass Bar, By.

Proceeding in this way each bar tested was several times twisted up to or beyond the elastic limit and the torque then diminished step by step back to zero. The position of the thermoelectric couple on the twisted bar was determined by a cathetometer mounted horizontally, parallel to the bar. Its position was read in each case with reference to a fixed scratch on the bar, thus avoiding any error due to a change in the relative position of bar and cathetometer.

Provision was made for comparing at each step the electrical resistance of a definite portion of the twisted bar with that of a similar portion of the other bar. The conditions were, of course, extremely unfavorable for an accurate comparison of electrical re-

sistances. The total resistance of the bars compared was only a few ten-thousandths of an ohm and the fact that the two ends of the bars were at widely different temperatures added another difficulty to the problem. Nevertheless, it seemed desirable to measure as accurately as possible the changes in electrical conductivity which might be expected to accompany any changes in thermal conductivity due to torsion. The method employed was the same as that used in the previous experiments.

All the bars used were round, five sixteenths of an inch in diameter and  $4\frac{1}{2}$  feet long.

#### RESULTS.

Observations were made on two bars of soft steel, two of iron, two of copper and one of brass. The observations on each bar were repeated four or more times on different days. In each case the results obtained from observations on different bars of the same material were substantially the same. Hence the results for only one bar of each material used are recorded in the following tables. The largest variation in electrical resistance was found in the bars of soft steel. In all the other materials employed this change was less than one part in two thousand and was less than the experimental error. Hence no figures are recorded for the change in the electrical conductivity of iron, copper and brass. In the tables T is used to designate the torque;  $\theta$ , the angle of twist; l, the distance from the copper clutch to the thermo-electric couple on the twisted bar; R, the resistance on the standard resistance box (proportional to that of the twisted bar); k, the ratio of the thermal conductivity of the bar to its conductivity before being twisted (proportional to  $l^2$ ); x, the corresponding ratio of electrical conductivities. express the torque in gram-centimeter units, the numbers recorded under T must be multiplied by 7,670.

The variations in the thermal conductivity of the four bars are shown in the accompanying curves.

TABLE I. Steel Bar,  $B_{19}$ . Nov. 22. Tem. 214°.

T ÷ 7670	θ	2	R	Α'	The second control of
0	0°	48.24 cm.		1.0000	
32	42	48.16	Resistance	.9970	
64	87	47.82	not	.9828	
82	107	47.33	measured.	.9626	
0	2	47.60		.9738	
	normalis areas de la republica de la composição de la com	Dec. 11.	Tem. 214°.	White Arms and the Committee of the	
0	2	47.69	Resistance	.9772	The second secon
32	42	47.40	not	.9656	
64	88	46.97	measured.	.9480	
0	3	47.47		.9682	
		Dec. 16.	Tem. 214°.		
0	2	47.86	2104.3	.9841	1.0000
32	41	47.58	2106.1	.9729	.9992
64	86	47.44	2106.9	.9673	.9988
82	111	47.15	2108.0	.9553	.9982
40	76	47.41	2106.0	.9661	.9992
0	4	47.72	2105.8	.9785	.9993
		Dec. 17.	Tem. 214°.	\$ 100 miles (100 miles	
0	3	47.80	And the second section of the s	.9819	The second section of the second second second
32	40	47.32	Resistance	.9622	
64	89	47.14	not	.9549	
82	116	47.07	measured.	.9519	Į.
40	83	47.28		.9605	A CONTRACTOR OF THE PARTY AND
		Jan. 7.	Tem. 213°.		
0	6	47.94	2104.9	.9875	.9997
32	43	47.44	2105.2	.9673	.9996
64	90	47.03	2105.0	.9501	. 9997
82	116	46.74	2106.8	.9390	.9988
0	6	47.30	2104.2	.9613	1.0000
		Jan. 9.	Tem. 213°.		
0	5	48.07	2104.4	.9927	1.0000
U	43	47.47	2105.0	.9686	.9997
32		1	2106.0	.9618	,9992
- 1	90	47.31	2100.0		
32	90 116	47.31 46.94	2106.8		
32 64	- 1			.9472 .9579	.9988

Jan. 13. Tem. 213°.

-					
0	6	47.82		.9828	
64	90	47.29	2105.7	.9609	.9993
90	136	46.89	2106.8	.9450	.9988

TABLE II.

Iron Bar, B<sub>11</sub>.

March 24. Tem. 217°.

T÷ 7670	θ	Z	K
0	00	49.48 cm.	1.0000
16	24	49.36	.9951
29	58	49.21	.9890
16	45	49.41	.9971
	M	farch 25. Tem. 217°.	
0	25	49.70	1.0090
16	45	49.38	.9959
29	83	49.08	.9841
0	50	49.25	.9910
	N.	farch 26. Tem. 215°.	
0	49	49.69	1.0086
16	70	49.38	.9959
29	89	49.13	.9861
16	78	49.20	.9890
0	55	49.54	1.0025
under the desire of the control of t	N	farch 27. Tem. 214°.	
0	55	49.80	1.0131
16	77	49.59	1.0045
29	95	49.19	.9882
16	82	49.46	.9992
0	60	49.62	1.0055

TABLE III.

Copper Bar, B<sub>14</sub>.

March 4. Tem. 194°.

 T + 7670	θ	Z	K
0	0°	52.76 cm.	1.0000
12	29	52.62	.9950
24	134	52.11	.9756
12	112	52.22	.9799
0	72	52.38	.9856
1			AND RESIDENCE OF THE PROPERTY

	1 8	March 5. Tem.	. 194°.	
- 0	72	52.3	31	.9831
12	107	52.1	16	.9774
22	194	51.7	78	.9633
12	178	51.8	38	.9669
0	142	51.9	90	.9680
it system halfes emperer e en may teluge interessionely a preservant floridate come	λ	Iarch 10. Tem	. 194°.	The second secon
0	141	51.9	99	.9713
12	169	51.9	92	.9687
24	245	51.5	58	.9558
12	227	51.7	79	.9637
0	190	51.8	83	.9651
and the second second second second second	1	Jarch 11. Tem	ı. 194°.	and defined on the 21 Mg
0	189	51.9	92	.9687
12	217	51.7	79	.9637
24	257	51.7	74	.9619

TABLE IV.

Brass Bar, B<sub>17</sub>.

Feb. 22. Tem. 204°.

management on improvement or other		Control of the Control of the State of the S	eminentalistica un esta su con de la constanta
T + 7670	θ		K
0	0°	48.90 cm.	1.0000
16	47	48.49	.9874
32	118	47.88	.9626
16	107	47.88	.9626
0	25	48.32	.9807
	Feb. 2	4. Tem. 204°.	
0	25	48.61	.9924
16	63	48.15	.9740
32	119	47.88	.9626
16	90	47.99	.9672
0	29	48.41	.9844
	Feb. 2	25. Tem. 204°.	
0	29	48.53	.9891
16	70	48.15	.9740
32	129	47.83	.9609
16	104	47.91	.9639
0	32	48.18	.9748
	Feb. 2	28. Tem. 204°.	
0	32	48.48	.9874
16	76	48.06	.9698
32	. 126	47.88	.9626
16	106	48.04	.9694
- 0	37	48.42	.9849

## Conclusions.

It will be observed that in all cases the thermal conductivity is diminished by torsion; that the recovery is not complete when the torque is removed, even though no permanent twist has been produced; that the thermal conductivity tends to regain its original value after a period of rest; that the change is greatest in the case of steel where the torque applied is the greatest and where also the change in electrical conductivity is most marked. The maximum change produced at any one time in the thermal conductivity of steel is from 3 to 5 per cent. The corresponding change in its electrical conductivity is from .1 to .2 per cent. The maximum changes produced in the thermal conductivity of iron, copper and brass are from 1 to 3 per cent. while the corresponding changes in their electrical conductivity are less than one twentieth of one per cent.

It seems probable that a linear relation exists between the thermal conductivity and the angle of twist. This is brought out most clearly in the curves for copper where the experimental points fall almost exactly on parallel straight lines. A similar relation is rather closely approximated in most of the curves for the other metals. As the strain in a bar approached the elastic limit, the twist ceased to be uniformly distributed but took place largely at one point while the torsion in the rest of the bar may have actually diminished. An attempt was always made to increase the torsion just as long as the twist was uniformly distributed through the bar. It was not always possible to tell when this limiting condition was reached. The apparent variation in the thermal conductivity of the same bar under the same conditions of strain on different days is probably due in part to a change in the radiating power of its surface.

In all of these experiments the torque acted in the same direction. It would be a matter of interest to observe the effect of twisting a bar first in one direction and then in the other. From these experiments and those of the preceding paper it is apparent that any theory which fully explains the processes of thermal and electrical metallic conduction must account for a series of changes in thermal conductivity due to mechanical strains whose magnitude is far greater than that of the corresponding changes in electrical conductivity.

OLIVET COLLEGE, April, 1909.

# THE DISTRIBUTION OF ENERGY IN THE SPECTRUM OF THE TUNGSTEN FILAMENT.

By R. E. NYSWANDER.

THE increased luminous efficiency of metallic filament lamps over the carbon incandescent lamp, has led to the investigation of the source of this increased energy, whether it is due in part to greater selective radiations in the visible spectrum or to the increased temperature at which it is normally burned. In fact, either of these causes alone would be sufficient to account for the increased efficiency, or it might be contributed to the combined effects of both. All radiating bodies at high temperatures follow approximately, the general laws of radiation, and since radiant energy in the visible spectrum is small, it would not be expected to find substances of unusually large emissivity in this region.

A theoretical consideration of black body radiations shows that the radiant efficiency varies with the temperature of the radiator, and from experimental investigations, this is in general true for all sources of radiation. Grau found for the luminosity curves of carbon and tungsten, that with increasing temperatures the curves approach each other and probably intersect between 1800° and 1850° C. With lower temperatures the watts per candle-power are somewhat less for the metallic filament lamps than for the carbon filament lamps. For temperatures above this point of intersection the efficiency of the carbon filament lamp would even be higher than the tungsten lamps. It was concluded that the higher economy of the tungsten lamps is due to the higher temperature of its filament. The normal burning temperature of the tungsten lamp is about 1850° C. while for the carbon lamp it is about 1660° C. At these temperatures the tungsten filament is three times as bright as a carbon filament, so that the increased efficiency was readily accounted for. Waidner and Burgess2 concluded that a

<sup>&</sup>lt;sup>1</sup> Elek. und Masch., 25, 295, 1907.

<sup>&</sup>lt;sup>2</sup> Electrical World, 48, 917, 1906.

considerable part of the gain in efficiency in the metal filament over the carbon filament is due to the higher working temperature at which it may be operated.

In the present investigation the distribution of energy in the spectrum of the tungsten filament, for various temperatures, was determined by means of a reflecting spectrometer, and radiometer.

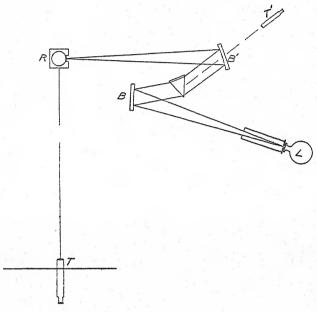


Fig. 1.

The spectrometer and radiometer have been described by the author  $^1$  in a previous paper. The arrangement of apparatus is shown in Fig. 1. A fluorite prism of clear quality and free from flaws was at hand. Its refracting angle measured  $38^{\circ}$  59′ 29″ and its faces were  $2.5 \times 3$  cm.

The lamp L was one of the early commercial types, but furnished with a side tube with a ground face upon which was sealed a fluorite window, and with an exhaustion tube. Since the prism table of the spectrometer was not provided with a graduated circle it was necessary to use the method of constant angle of emergence. The lamp was rigidly attached to the collimating arm of the spectrom-

eter, and adjusted so that the filament was parallel to the slit, and in line with the center of the concave mirror B. The same filament was used throughout the work, and all radiations except those from this single filament were screened.

The dispersion curve of the fluorite prism was computed from the values of the indices of refraction given by Paschen. The angle of emergence was the angle of minimum deviation of the sodium lines. The prism was accurately adjusted for minimum deviation by use of the telescope T' which was placed in line with the deviated rays from the prism.

The spectrometer and radiometer were completely covered by screens to protect them from external radiations.

No shutter was used, but deflections were produced by turning on the light, with a switch at the side of the observer, just long enough to produce a deflection of the vanes. The zero was determined by taking the mean of the scale readings before and after the exposure. The scale T was placed 120 cm. from the radiometer R. The sensibility of the radiometer, as previously defined by the author, 2 was 12.5. Deflections were read to .01 cm.

No trouble from air leaks was experienced, so that a complete radiation curve could be obtained under constant conditions.

The current source was supplied by a 110-volt dirrect-current circuit of excellent voltage regulation, yet, to insure greater uniformity, a storage battery was connected in multiple with the dynamo circuit through a tin resistance. The lamp current was taken from points on the tin resistance between the terminals of the storage battery.

## RESULTS.

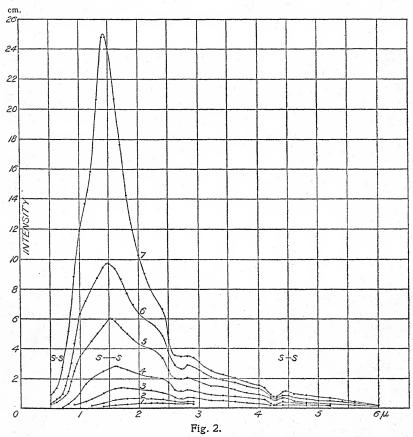
The series of curves in Fig. 2 were obtained for values of  $\lambda_{max}$  as follows: 1, 2.3  $\mu$ ; 2, 1.9  $\mu$ ; 3, 1.7  $\mu$ ; 4, 1.61  $\mu$ ; 5, 1.52  $\mu$ ; 6, 1.475  $\mu$ ; 7, 1.425  $\mu$ ; with corresponding black-body absolute temperatures of 1278°, 1547°, 1729°, 1826°, 1934°, 1994°, 2063°, respectively. All curves have been corrected for width of slit by the following equation of Paschen.<sup>3</sup>

(1) 
$$\alpha f(x) = F_{(x)} - \frac{1}{6}F_{1(x)} + \frac{2}{4^{5}}F_{2(x)} - + \cdots$$
<sup>1</sup> Ann. der Phys., 56, 765, 1895.

<sup>2</sup> Loc. cit.

<sup>3</sup> Ann. der Phys., 60, 712, 1897.

The width of both the spectrometer and radiometer slits was .3 mm. equivalent to 3' of arc on the spectrometer circle. This width (s-s, Fig. 2) was sufficiently small that it was not necessary to carry



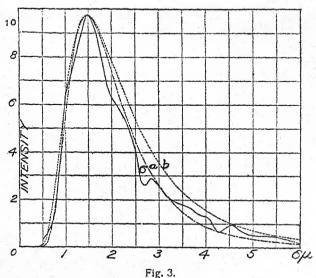
the correction further than the second term of equation (1), even in the most intense part of the spectrum. Beyond 1.8  $\mu$  the correction was so small that the first term only was used.

Assuming Wien's law

$$E = c_1 \lambda^{-\alpha} e^{-\frac{c_0}{\lambda T}}$$

to hold for all values of the radiating constant, we may by the method of Paschen <sup>1</sup> determine an approximate mean value of  $\alpha$  for <sup>1</sup> Ann. der Phys., 58, 487; 60, 664, 1897.

any emission curve, independent of the temperature of the radiator. For the tungsten filament a value of the radiation constant  $\alpha=6.53$  was obtained from curve 6, using the mean of six independent determinations. With this value of  $\alpha$  a normal radiation curve for tungsten was constructed from Wien's law, and likewise a black-body curve was computed, and the three, all of which have equal values of



 $\lambda_{\max}$  and  $E_{\max}$  have been plotted together for comparison in Fig. 3. The deviations of the actual tungsten curve from the normal radiator a, will indicate the radiation peculiarities of the tungsten filament. This deviation is prominent in the visible spectrum where the tungsten curve shows strong selective radiation. At .5  $\mu$  the tungsten filament radiates less than normal, but at 1  $\mu$  it radiates like a blackbody of the same value of  $\lambda_{\max}$ . In the regions 1.3  $\mu$  and 1.5  $\mu$  to 3  $\mu$  tungsten shows less than normal radiation, however, beyond 3  $\mu$  it radiates more than curve a, and at 4.6  $\mu$  and 5  $\mu$  the value of a is nearly equal to that of a black body. The characteristics of curve 6 are present in the curves of Fig. 2, except those of small intensity.

### LUMINOUS EFFICIENCY.

From Wien's law we may write for a complete radiator

(2) 
$$\int_{J_1}^{J_2} dJ = c_1 \int_{\lambda_1}^{\lambda_2} \lambda^{-5} e^{-\frac{c_2}{\lambda T}} d\lambda$$

which can readily be integrated by the method of integration by parts, if a simple substitution  $z=-c_2/\lambda T$  be made, and finally reduces to

$$[J]_{J_1}^{J_2} = \frac{c_1 T^4}{c_2^4} \left[ e^{-\frac{c_2}{\lambda T}} \left( \frac{c_2^3}{\lambda^3 T^3} + \frac{3c_2^2}{\lambda^2 T^2} + \frac{6c_2}{\lambda T} + 6 \right) \right]_{\lambda_1}^{\lambda_2}.$$

If for  $c_2$  its value  $5\lambda_{\max}T$  be substituted in (3) the resulting equation (4) becomes independent of temperature.

(4) 
$$[J]_{J_1}^{J_2} = \frac{c_1}{5^4 \lambda_{\max}^4} \left[ e^{-\frac{5\lambda_{\max}}{\lambda}} \left( \frac{5^3 \lambda_{\max}^3}{\lambda^3} + 3 \frac{5^2 \lambda_{\max}^2}{\lambda^2} + 6 \frac{5\lambda_{\max}}{\lambda} + 6 \right) \right]_{\lambda_1}^{\lambda_2}$$

When  $\lambda_1 = 0$  and  $\lambda_2 = \infty$  we have a value for the total energy of radiation  $J = aT^4$  which is Stefan's law in which the constant  $a = 6c_1/c_2^4$ .

Assuming the visible spectrum to lie between the limits  $\lambda_1 = .4 \,\mu$  and  $\lambda_2 = .76 \,\mu$ , the radiant efficiency of a black body may be expressed as follows:

pressed as follows:
$$\frac{\int_{.4\mu}^{.76\mu} \lambda^{-5} e^{-\frac{5\lambda_{\text{max}}}{\lambda}} d\lambda}{\int_{0}^{\infty} \lambda^{-5} e^{-\frac{5\lambda_{\text{max}}}{\lambda}} d\lambda}.$$
(5)
Rad. eff. = 
$$\frac{\int_{.4\mu}^{.76\mu} \lambda^{-5} e^{-\frac{5\lambda_{\text{max}}}{\lambda}} d\lambda}{\int_{0}^{\infty} \lambda^{-5} e^{-\frac{5\lambda_{\text{max}}}{\lambda}} d\lambda}.$$

$$\frac{\lambda_{\text{MAX}} = 1.2}{\lambda_{\text{MAX}} = 1.2} \frac{1.4}{1.4} \frac{1.6}{1.635} \frac{1.8\mu}{1.635}$$
Fig. 4.

In Fig. 4 is shown the luminous efficiency of a complete radiator for varying values of  $\lambda_{max}$  and corresponding absolute temperatures. The luminous efficiencies of the tungsten curves 5, 6

and 7 are 1.5, 1.4 and 2.0 per cent. respectively, while the radiant efficiencies of a black body for corresponding values of  $\lambda_{max}$  are approximately 1.03, 1.28, 1.65 per cent. The efficiency of curve  $\alpha$ , Fig. 3, is only 0.85 per cent. Since this curve and no. 6 of the tungsten have practically equal areas, for this value of  $\lambda_{max}$  the selective radiation of the tungsten filament in the visible spectrum is more than 1.6 times normal. The radiant efficiencies as given or the tungsten filament have been integrated directly from the curves, correcting only for the bands at 2.7  $\mu$  and 4.26  $\mu$ . These bands agree in position with the atmospheric absorption bands of CO<sub>2</sub> gas, and a smooth curve was substituted across them in measuring the areas with the planimeter. The curves were extrapolated from .5  $\mu$  to .4  $\mu$ .

The method of determining the radiant efficiency from the ratio of the luminous area to the total area is subject to various criticisms, not only because of errors in slit width corrections but also from selective absorption of the prism, and windows of the lamp and radiometer, and from variation in the reflecting power of the spectrometer mirrors for various wave-lengths. The correction for slit width undergoes very rapid changes in the visible region of the spectrum and possible errors may be introduced. In this work no correction was made for absorption of the rock-salt windows of the radiometer or for the absorption of the fluorite prism or the fluorite window of the lamp. Nichols and Coblentz 1 found that rock-salt was much less transparent for shorter than for longer wave-lengths. Mendenhall<sup>2</sup> added a correction of 7.8 per cent, of the observed efficiency to correct for the absorption of the fluorite window. The reflecting power of the silver mirrors is also less for short waves than for the longer wave-lengths. Paschen 3 has shown that this difference is greater after the mirror, through age, has taken on a brownish tint. The mirrors of the spectrometer used by the author were several years old and somewhat discolored,

Due to the possible corrections which might be applied the recorded values of efficiencies of the tungsten lamp are somewhat

<sup>&</sup>lt;sup>1</sup> Phys. Rev., 17, 270, 1903.

<sup>&</sup>lt;sup>2</sup> Phys. Rev., 20, 162, 1905.

<sup>&</sup>lt;sup>3</sup> Ann. der Phys., 309, 305, 1901.

too small. Yet, these values cannot be compared directly with the earlier determination of luminous efficiencies, since these earlier methods were subject to large errors due to incompleteness of absorption of the absorbing cells. According to Ångström 1 these earlier values of radiant efficiencies are from two to three times too high.

Physical Laboratory, Cornell University, August, 1908.

<sup>1</sup> Astrophys. Jour., 15, 226, 1902.

# A SIMPLE INTERFEROMETER FOR SHOWING THE ZEEMAN EFFECT.

By A. H. Prund.

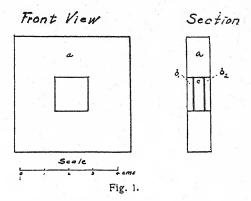
IN order to show the Zeeman effect and the structure of spectral lines, instruments of high resolving power are necessary. Such instruments (echelon, grating, Fabry and Perot interferometer, etc.) are rather expensive and sometimes difficult to adjust - hence the above-mentioned phenomena are not often seen by students in optics. Several years ago I made an extremely simple and inexpensive interferometer of high resolving power for lecture-room demonstrations. At the time no thought was given to publishing an article on the subject and later it was found that Lummer 1 had already constructed an instrument of this type. However, at a recent meeting of the Physical Society, the Zeeman effect was shown by means of this instrument and since then a considerable number of letters, asking for information, has been received. Feeling that there was a real demand for an interferometer which at the same time was efficient, inexpensive and always in adjustment, I have thought it worth while to present a note on the subject.

The instrument is, in reality, a simplified Fabry and Perot interferometer. Its construction may, perhaps, best be understood from Fig. 1 in which a is a wooden block with a square opening in the center to receive the optical system. The glass plate c is optically plane-parallel and about 3 mm. thick.<sup>2</sup> It is silvered on both sides, so as to be still slightly transparent, and is protected by the plates  $b_1$  and  $b_2$  which are cemented on with Canada balsam. While these two cover plates need not be optically perfect, they ought to be made of good crystal-plate glass. The efficiency of the instrument depends largely upon the thickness of the silver films on plate c—and the best thickness can be found only by trial. A good method

<sup>&</sup>lt;sup>1</sup> Lummer, Arch. Néerl. (2), 6, p. 773, 1901.

<sup>&</sup>lt;sup>2</sup> Such a plate may be obtained from the optical works of Mr. O. L. Petitdidier or Mr. J. A. Brashear.

of procedure is to place the plate c and two other (trial) plates in a bowl-shaped vessel and to silver all three by means of the Rochelle salt silvering solution to such a degree that considerably more than 50 per cent. of the light is reflected from a single surface. Next the silver is removed from one of the two surfaces of each of the trial plates and the remaining silvered surfaces are polished by a process to be described shortly. Upon placing these two reflecting



surfaces together in such a way as to enclose a wedge-shaped film of air, an ordinary gas flame is viewed through the system and a series of images, due to multiple reflections, are seen. The silver films are of the proper thickness when the number of images is 18 or more. Since the plate c has the same thickness of coating as the two trial plates, it is only necessary to polish its two silver films and to attach the plates  $b_1$  and  $b_2$ . Upon mounting this system of plates in the block a the interferometer is completed.

In order to polish the films I have found it advisable to dry them first for about 15 minutes in an air-bath heated to 40° or 50° C. The first stage of polishing is carried out by means of a toilet "powder-puff" covered with optical rouge. The ivory handle of the puff is gripped in the chuck of a drill-press or lathe and the arrangement is used as a buffing-wheel. This procedure seems to harden the film as it is found that further polishing may be carried out by means of a piece of very smooth kid leather, covered with rouge. Given a film of proper thickness, the process of polishing increases the reflecting power to such an extent that the number of multiple reflections is about doubled.

As a source of light, the luminous vapors of mercury, helium and cadmium have been found very serviceable. A helium tube (containing the gas under a pressure of about 2 mm.) is very convenient for showing the Zeeman effect; on the other hand, mercury and cadmium lamps serve well in a study of the structure of spectral lines. The Cooper-Hewitt lamp serves excellently as a source of mercury lines. If such a lamp is not available, it is an easy matter to construct one according to the designs given by Rentschler<sup>1</sup> and the writer.<sup>2</sup> In order to isolate any desired line by means of color-screens, it is only necessary to consult the "Atlas of Absorption Spectra" in order to find a suitable combination of absorbing substances. In order to isolate the green mercury line ( $\lambda = 5461$ ) I have found it convenient to use a mixture of nitrosodimethyl aniline (to cut out the blue lines) and neodymium nitrate (to cut out the yellow lines).

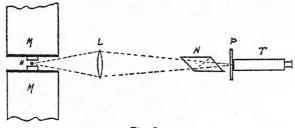


Fig. 2.

The arrangement of apparatus for showing the Zeeman effect is given in Fig. 2 where H is a helium tube placed between the poles of an electro-magnet M. By means of a lens L, the light, after passing through the Nicol prism N, is concentrated on the interferometer P which is rigidly attached to a telescope or opera glass T (focused on infinity). The magnifying power of the telescope ought to be from 2 to 4 diameters. To show the effect, a strength of field of 5,000 Gauss is ample. It is advisable to insert a rheostat into the circuit exciting the magnet and to increase the current gradually until the effect is at its best.

<sup>&</sup>lt;sup>1</sup> Rentschler, Astrophys. Jour., 5, p. 353, 1908.

<sup>&</sup>lt;sup>2</sup> Pfund, Astrophys. Jour., 4, p. 296, 1908.

<sup>&</sup>lt;sup>3</sup>Uhler and Wood, Carnegie Institution (1907).

Although the instrument possesses the obvious disadvantage of a fixed resolving power, it nevertheless justifies its existence by being efficient, inexpensive and always in adjustment.

Johns Hopkins University, March, 1909.

## PROCEEDINGS

#### OF THE

# AMERICAN PHYSICAL SOCIETY.

## MINUTES OF THE FORTY-SEVENTH MEETING.

THE spring meeting of the Physical Society was held in Washington, D. C., on Monday, April 26, and Tuesday, April 27, 1909.

On Monday, April 26, the sessions were held at the Cosmos Club.

The Tuesday sessions were held at the Bureau of Standards.

Vice-President W. F. Magie presided.

On the recommendation of the Council Article I. of the by-laws was suspended and Professor Max Planck, of Berlin, was elected an honorary member of the society.

The following papers were presented:

The Exponent of Gas Radiation. W. J. HUMPHREYS.

The Distribution of Gases in the Atmosphere. W. J. HUMPHREVS.

Note on the Rate of Movement, Depth and Intensity of Storms. WM. R. BLAIR.

The Variation of Temperature with Altitude in the Lower Stratum of the Atmosphere and its Relation to Surface Air Pressure and other Phenomena. WM. R. BLAIR.

Stationary Clouds to the Leeward of Hill and Mountain Ranges. WM. R. BLAIR and L. C. Ross.

On the Earth's Magnetic Variations. (By title.) L. A. BAUER.

The Effect of Temperature and Pressure on Rigidity and Viscosity. (By title.) A. A. Michelson.

Applications of Probability to Mechanics and Thermodynamic Analogies for a Simple Dynamical System. (By title.) EDWIN B. WILSON.

The Sublimation of Ice. H. T. BARNES and W. S. VIPOND.

Specific Heats at High Temperatures. W. P. WHITE.

Calorimetric Accuracy. W. P. WHITE.

The Critical Density of Water. HARVEY N. DAVIS.

Re-determination of the Radiation Constants of a Black Body. (By title.) W. W. COBLENTZ.

On the Scale of the Platinum Thermometer. C. W. WAIDNER and G. K. Burgess.

The Specific Heats of Gases at Low Temperatures. J. S. Shearer.

The Retardation of Alpha Rays by Metals and Gases. T. S. Taylor. On  $\alpha$  Rays from Radium B. Howard L. Bronson.

The Kinetic Energy of the Positive Ions from Hot Bodies. F. C. Brown.

The Absence of Photoelectric Fatigue at Very High Vacua. (By title.) R. A. MILLIKAN and G. WINCHESTER.

Preliminary Note on the Variation with Speed in the Mass of an Electron. C. A. Proctor.

The Rotatory Power of Limonene at Low Temperatures. F. A. Molby.

The Efficiency of Light of Different Wave-Lengths in Exciting Fluorescence. E. L. NICHOLS and ERNEST MERRITT.

The Electrical and Optical Properties of Metallic Selenium. A. H. Pfund.

The Effect of Temperature upon the Absorption Spectra of Various Salts in Solution. W. W. Strong.

An Improved Form of the Duddell Singing Arc. (By title.) G. W. NASMYTH.

On the Reproducibility of the Clark and Weston Cells, and a Recalculation of the Mechanical Equivalent of Heat. H. L. Bronson and A. N. Shaw.

The Determination of the Constants of Instrument Transformers. P. G. Agnew and T. T. Fitch.

The Daylight Efficiency of Artificial Light Sources. HERBERT E. IVES.

Incandescent Electric Lamps as Secondary Photometric Standards. E. B. Rosa and G. W. MIDDLEKAUFF.

Note on the New Value of the Unit of Candlepower of the Bureau of Standards. E. B. Rosa.

Methods and Errors in Magnetic Measurements. Charles W. Burrows.

On the Absolute Measurement of Current by a New Current Balance. E. B. Rosa and N. E. Dorsey.

Preliminary Report on the Alternating Current Method of Measuring Resistance in Absolute Measure. E. B. Rosa and F. W. Grover.

An Experimental Determination of the Resolving Power Constant of Lenses. P. G. NUTTING.

The Natural Scale of Pure Color. (By title.) P. G. NUTTING.

An Optical System of Obtaining Monochromatic Light. (By title.) Frederick Bates.

The Change of Electrical Resistance with Temperature in the case of Palladium Charged with Hydrogen. E. C. CRITTENDEN.

The Resistance of the Alkali Metals at Low Temperatures. R. C. RODGERS.

Achromatism of Interference. C. W. CHAMBERLAIN.

Ernest Merritt, Secretary.

## On a Rays from Radium B.1

By Howard L. Bronson.

SOME time ago the writer, investigated the question as to whether or not radium B gave out  $\alpha$  particles. The conclusion reached was that no  $\alpha$  particles were shot off with sufficient velocity to ionize the air. Recently the question has again been raised by Frederic A. Harvey, who concludes that a large part of the ionization produced by the active deposit from radium is due to  $\alpha$  particles from radium B, whose ionizing range in air lies between 2.6 and 3.0 mm.

The method employed by Harvey was a modification of that used by Bragg and Kleeman.<sup>4</sup> The writer has repeated this experiment but has been unable to get any indication whatever of the presence of such short range  $\alpha$  particles as Harvey describes. The method at best, however, is not well adapted for investigating very short range  $\alpha$  particles. I have, therefore, tried a new method which avoids most of the difficulties inherent in the previous one. The principle of the method is very simple and avoids the necessity of changing the distance between the testing vessel and the active material. Instead the range of the  $\alpha$  particles is gradually increased by reducing the pressure of the air.

In the arrangement of the apparatus used by the writer, the two plates of the testing vessel were about 5 mm. apart, and the lower one, which was of wire gauze, was about 5 mm. above the active wire. Now, if none of the  $\alpha$  particles present had a range of less than 10 mm. in air at atmospheric pressure, then the ionization current should vary as the pressure. If, however, radium B gives out  $\alpha$  particles which have a range of 2.5 mm., and if they produce the same number of ions per cm. of path as the  $\alpha$  particles from radium C, then, after the pressure is reduced to half an atmosphere, the short range  $\alpha$  particles will begin to enter the testing vessel, and the ionization will remain constant until the pressure has fallen to a quarter of an atmosphere. At this point the path of the  $\alpha$  particles will extend through the entire depth of the testing vessel, and as the pressure is still further reduced, the ionization again becomes proportional to the pressure.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

<sup>&</sup>lt;sup>2</sup> Phil. Mag., 11, 680, 1906.

<sup>&</sup>lt;sup>3</sup> Phys. Zeit., 10, 46, 1909.

<sup>4</sup> Phil. Mag., 10, 318, 1905.

The results of the experiment showed that the ionization in the testing vessel was approximately proportional to the pressure of the air from 76 to 3 cm. It would, therefore, seem fair to conclude that there is not present in the active deposit from radium any substance giving out  $\alpha$  particles which have a range in air between 1 and 5 mm.

MACDONALD PHYSICS BUILDING, MCGILL UNIVERSITY, MONTREAL, April, 2, 1909.

## THE SUBLIMATION OF ICE.1

By H. T. BARNES AND W. S. VIPOND.

MEASUREMENTS of the latent heat of sublimation of ice have been made by means of the Bunsen ice calorimeter. When the ice was evaporated rapidly the value was found to be identical with the latent heat of vaporization of water at o° C. as determined by Regnault and A. W. Smith. When the ice was evaporated slowly the latent heat was what would be expected as the sum of the latent heats of vaporization of water and fusion of ice. Intermediate values could be obtained by regulating the rate of the evaporating air current.

The theory is advanced that ice vaporizes in a polymeric form which is unstable, rapidly breaking down into water vapor with the absorption of 80 calories of heat per gram. With rapid currents of air passed through the calorimeter the vapor was removed before having time to break down, while with slow currents the transformation took place entirely within the calorimeter.

On the Reproducibility of the Clark and Weston Cells, and a Recalculation of the Mechanical

EQUIVALENT OF HEAT.1

By H. L. Bronson and A. N. Shaw.

THE investigation described in this paper was undertaken with a double purpose: (1) to determine with what accuracy we could reproduce Clark and Weston standard cells by following specifications given by Wolff and Waters;<sup>2</sup> (2) to compare these cells with those made according to the old specifications and thus to correct the value which Dr. Barnes obtained for the mechanical equivalent of heat and which was based on the assumption that the Clark cell at 15° C. had a value of 1.4342 int. volts.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

<sup>&</sup>lt;sup>2</sup> Bulletin of Bureau of Standards, Vol. 4, 1, 1907.

This work was commenced last summer by Dr. Bronson at the Bureau of Standards. Several Clark and Weston cells were made by him there and compared with the reference cells at the bureau. Some of these were then brought by him to Montreal, and others have since been made by both of the writers. We have also been fortunate in having for comparison three Weston cells made last summer at the National Physical Laboratory in London. One of these was kindly presented and the other two loaned to us by Mr. Ormand Higman, director of the standardizing laboratory at Ottawa.

The agreement among the Weston cells seems to be rather better than among the Clark cells. Six Weston cells made by the writers have an average variation from their mean of less than 5 micro-volts, and our calculation shows that their mean is only about 2 micro-volts higher than the reference cells at the Bureau of Standards and about 6 micro-volts higher than the mean of the three cells from the National Physical Laboratory. In the case of the Clark cell the average variation from their mean is less than 10 micro-volts, while their mean is about 14 micro-volts higher than the reference cells at the Bureau of Standards. As a check upon the accuracy of these values, a direct comparison was made between the Clark and Weston cells. The ratio at 25° C. was found to be 1.394792, which is higher than the value 1.394780 found by Wolff and Waters by an amount which is exactly accounted for by the above mentioned differences between our cells and those made by them.

The above results indicate that both Clark and Weston cells can be readily reproduced with a much greater accuracy than has generally been supposed.

# ON THE MECHANICAL EQUIVALENT OF HEAT.

In 1902, Dr. Barnes 1 determined the absolute value of the mechanical equivalent of heat in terms of the international electric units. Taking the value of the true ohm as 1.01358 B.A. units and the value of the Clark cell at 15° C. as 1.4342 volts, he obtained 4.1888 as the mean value of the joules per calorie for the interval between 5° C. and 95° C.

Within recent years, however, several important determinations of the absolute value of the Clark cell have been made. The different determinations differ among themselves by several parts in 10,000, but I think we may fairly assume that 1.4330 volts is very near the true value. There are, however, important differences between these cells and those set up according to the old specifications by Dr. Barnes, and used by him in the determination of the mechanical equivalent of heat. Dr. Barnes has therefore made for us twelve cells according to the specifications which he formerly used, and we have compared these with our new cells. This

<sup>&</sup>lt;sup>1</sup>Phil. Trans. Roy. Soc., A, 199, 149, 1902.

comparison shows that these twelve cells average almost exactly .30 millivolt higher than the cells made according to the new specifications. This is also in accord with the measurements of Wolff and Waters on similar cells.

The best absolute value which can at present be taken for those cells which Dr. Barnes used in determining the mechanical equivalent is, therefore,

1.4330 + .0003 = 1.4333 volts at  $15^{\circ}$  C.

Dr. Barnes had recalculated his value of the mechanical equivalent on this basis, and has obtained 4.1835 joules per calorie for the interval between 5° and 95° C., or 4.1849 joules per calorie between 0° and 1c0° C. The value obtained by Reynolds and Moorby, for this same interval would be 4.1836 joules per calorie. The value which Rowland obtained by direct mechanical methods also shows remarkably good agreement with that obtained by Dr. Barnes by electrical methods. This is especially true when we consider that Rowland did not claim for his results an accuracy much greater than 1 part in 1,000. The mean value obtained by Rowland, as corrected by Weidner and Mallory, is 4.185 joules per calorie between 5° and 35° C., while Dr. Barnes' mean value for the same range is 4.183. The above results would indicate that the values assumed for the ohm and Clark cell cannot be far from the truth.

Macdonald Physics Building, McGill University, Montreal, April 7, 1909.

Incandescent Electric Lamps as Secondary Photometric Standards.<sup>2</sup>

By E. B. Rosa and G. W. MIDDLEKAUFF.

In the absence of a satisfactory primary photometric standard which is sufficiently reliable and reproducible as to be generally adopted it is customary in the measurement of the light of electric illuminants, and to some extent in gas flames, to use carbon filament incandescent electric lamps as secondary standards.

The Bureau of Standards has maintained its unit of light substantially constant for six years by this means, and has made frequent intercomparisons with foreign laboratories in this way. In order to increase the precision of photometric measurements it is desirable that standards be used which are substantially of the same color as the light being measured, and this makes it necessary to have standards of different temperatures. For

<sup>1</sup> Monthly Weather Review, 35, 458, 1907.

<sup>&</sup>lt;sup>2</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

temperatures higher than can be attained with carbon lamps, metal filament lamps may be used in the same way, and recent experiments show that such lamps may be seasoned and used in such a way as to be satisfactory as standards of candlepower.

We have recently improved our methods of seasoning and testing lamps which are to be used as standards, so as to make them even more reliable and more permanent than heretofore. Some of the advantages of these standards over flame standards will be pointed out in the paper, and the possibility of using such secondary standards for maintaining permanently the common unit of light will be discussed.

PRELIMINARY REPORT ON THE ALTERNATING CURRENT METHOD OF MEASURING RESISTANCE IN ABSOLUTE MEASURE.<sup>1</sup>

BY E. B. ROSA AND F. W. GROVER.

THE value of a resistance in absolute measure is determined by the alternating current method by measuring the value of the self or mutual inductance of a coil by means of alternating currents in terms of resistance and time with sufficient precision. That is to say, assuming that an absolute inductance is known in terms of its dimensions, and that it can be compared with precision with some other coil which is to be measured by means of alternating currents, or that it can itself be measured by the alternating current method, it then remains to determine by means of some kind of a bridge or combination of resistances, the value of the self or mutual inductance by means of alternating current. We have done sufficient work on this subject to justify a preliminary report of results which was given at the meeting, although we are not as yet prepared to give any final values.

The precision of measurements of the inductances is satisfactory. Some improvement remains to be made in the primary inductances.

NOTE ON THE NEW VALUE OF THE UNIT OF CANDLEPOWER OF THE BUREAU OF STANDARDS.

By E. B. Rosa.

THE Bureau of Standards has recently come to an agreement with the National Physical Laboratory of England and the Laboratoire Central d'Électricité of Paris, whereby a common value of the unit of candlepower for these three countries is to be maintained by these laboratories acting together.

The Bureau of Standards, in order to come into agreement with the values of England and France, is reducing its unit of candlepower by

<sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

1.6 per cent. The effect of this will be to increase the candlepower ratings of lamps which are expressed in terms of the bureau unit, and this includes practically all of the electric lamps of the country.

Gas flames have been rated in terms of various flame standards, but the American Gas Institute has agreed to adopt the new unit of the bureau, so that hereafter all flame standards may be expressed in terms of the unit of the bureau.

This international candle will have a value one ninth greater than the Hefner unit, that is, the Hefner is 90 per cent. of the new unit of candlepower.

The International Electrotechnical Commission is undertaking to secure international sanction for the use of the term *international candle* for the common unit which is to be maintained constant by America, France, and Great Britain. There will then be two international units of light, the international candle, and the Hefner unit, having a simple ratio of 10:9.

# On the Absolute Measurement of Current by a New Current Balance.<sup>1</sup>

By E. B. Rosa and N. E. Dorsey.

THE Raleigh form of balance has been adopted as affording the possibility of determining the constant of an instrument with extreme precision, and giving a sufficiently large force to be measured accurately. Many improvements have been made over the original balance as used by Lord Raleigh, one of the most important being the use of water cooling to maintain the coils at constant temperature, so that the constant of the instrument and the forces to be measured are unaffected by the heat due to the current.

The instrument has been in use for more than a year, and has been investigated very elaborately for the purpose of obtaining the highest possible precision in the absolute measurement of current. The final results have not yet been obtained, but a report of progress will be made and the results communicated.

The difference found between the present legal value of standard cells and the value given from the current balance and a standard resistance is 9 parts in 10,000, giving the Weston Normal cell the value 1.0182 volts at 20° C. The corresponding value of the Clark Standard cell, as at present made, is 1.4324 at 15° C. (This is .0003 less than the older form of the Clark cell.) The value to one more decimal place will be given in the final account of the work.

<sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

THE DAYLIGHT EFFICIENCY OF ARTIFICIAL LIGHT SOURCES.1

By HERBERT E. IVES.

An investigation prompted by the question whether the newer high efficiency illuminants might not be screened to resemble daylight without prohibitive loss of efficiency. Daylight is assumed to have the spectral relation to acetylene found by E. L. Nichols' investigations. Two methods are developed. The first, by a discussion of the colored absorbing screens necessary to reduce a continuous spectrum to the daylight spectrum, and the luminosity values of the different colors of the spectrum, leads to a quantity

Intensity of white light obtained by screening source to daylight color
Intensity of unscreened source

called the "white light efficiency." The second, by considering the amount of white light which, mixed with a single spectrum ray, will

match the colored light, leads to a quantity

Intensity of white sensation called the "white sensation efficiency."

The white light efficiency depends upon arbitrary choice of point from which screening starts, and gives zero value to selective sources of the type of the mercury arc. It gives an indication of a source's suitability for use where color values are to be judged. Numerical values indicate that ordinary sources (glow lamps, acetylene, etc.) have from 20 to 50 per cent. available white light. A 1 1/4 watts tungsten lamp may be screened to resemble daylight with a resultant efficiency of about 4 watts per candle, or the efficiency formerly considered practical in electric lighting.

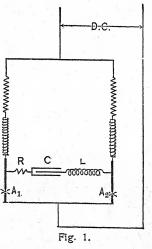
The white sensation efficiency is applicable to all types of sources, and accurately describes the color of the light or a white surface illuminated by it. It gives no idea of the source's suitability for color discrimination. It is, however, independent of any choice of screening point and scientifically preferable. The white sensation efficiencies are always higher than the white light efficiencies.

For the most useful comparison of artificial sources the results of the two methods have been combined by a graphical scheme. Rectangles represent the amounts of white sensation in the various sources, the shaded portions of the rectangles the amount of white light available by screening. Sources well suited for color discrimination have large shaded portion and vice versa, while large rectangles indicate lights of good integral color. The dominant spectrum hue of each light is given by an adjoining wave-length scale.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

An Improved Form of the Duddell Singing Arc. By George W. Nasmyth.

In the usual form of the Duddell singing arc, the direct current arc, in series with a suitable resistance and choke coil, has the oscillation circuit containing capacity and inductance connected in shunt across the arc, from anode to cathode. In the improved form, two arcs are used in parallel, each with its own resistance and choke coil, and the oscillation circuit is connected between the two anodes, the two cathodes being connected together. (Or the two anodes may be connected together, and the inductance and capacity placed between the two cathodes.) The diagram of connections for the new form is shown in the accompanying figure.



The chief advantages of this form of the singing arc are in the increased power available in the oscillation circuit, and a greatly increased stability in the oscillation conditions. The power available in the oscillation circuit is approximately twice that obtainable from the usual form of the singing arc. With two arcs connected in this way, the fluctuations in either arc have a tendency to be neutralized by the other arc, and the effect on the oscillations is greatly diminished. If the arcs are surrounded by a hydrogen atmosphere, supplied by alcohol lamps or illuminating gas, the oscillations will be maintained for a time even though one arc goes out, the other arc continuing to send the oscillations through the hydrogen atmosphere. If one arc is short circuited, the connections are changed to the usual form of the singing arc, and the oscillations will continue.

With this new form of the singing arc the author has obtained oscillations over a range of frequencies from two per second to 1,000,000 per

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society April 26 and 27, 1909.

second. As in the usual form, small currents' (from .5 to 3 amperes) give the most energy, and a water-cooled copper anode is of advantage. For low frequencies the arcs should be as long as possible, but for high frequencies it is necessary to shorten the arcs.

As in the Duddell form of the singing arc, the phenomena in this case may be explained as due to the negative slope of the voltage-current arc characteristic. Referring to the figure, suppose the current through the arc A, to be diminished by a small amount. The cross-section of the arc vapor will be decreased, thus increasing the resistance, and causing a rise in the potential difference across the arc. A charge will then flow through the condenser C of the oscillation circuit, causing an increase in the current through the arc A, the two choke coils keeping the two currents from the main supply constant. The increased current through  $A_n$  enlarges the cross-section of the arc, lowers the resistance of this arc, and decreases the potential difference across it. This causes more electricity to flow from the first arc into the condenser, raising the potential on the left-hand side of the oscillation circuit and lowering it upon the right, and so the effect goes on, cumulatively, until the potential difference across the condenser becomes great enough to reverse the process, and the oscillations go back and forth in the natural period of the oscillation ciruit.

Preliminary experiments with varying arc length and arc currents indicate that the equation for the frequency of the usual form of the singing arc holds also for the new form. This equation is

$$n = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c + \lambda l}{A}\right)^2}{4L^2}}$$

where L is the inductance, C the capacity and R the resistance in the oscillation circuit. I is the length of the arc, and e and d are constants depending upon the electrodes and the gas in which the arc is formed. For the new form, if  $I_1$  and  $I_2$  are the lengths and  $I_3$  and  $I_4$  the currents of the two arcs, respectively, the equation for the frequency would be

$$n = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c + l_1 d}{A_1} - \frac{c + l_2 d}{A_2}\right)^2}{4L^2}}.$$

If  $V_1$  and  $V_2$  are the potential differences across the two arcs, the equation may be written

$$n = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \frac{\left(R + \frac{dV_1}{dA_1} + \frac{dV_2}{dA_2}\right)^2}{4L^2}}.$$

1 See Phys. Rev., Vol. XXVII., No. 2, August, 1908, p. 128.

Experiments also indicate that the power available in the oscillations increases with -dV/dA, the negative slope of the arc voltage-current characteristic curve, and data which the author hopes to include in a more complete article in the near future show that in order to have the oscillations set up the resistance of the oscillation circuit must be less than the sum of the negative slopes of the two arc characteristic curves.

Physical Laboratory, Cornell University.

## SPECIFIC HEATS AT HIGH TEMPERATURES.1

### By WALTER P. WHITE.

YEAR ago, specific heat determinations at high temperatures were described in which the hot bodies were dropped from an electric furnace into a calorimeter. The calorimetric errors were negligible. The heat loss in transit was compensated and thus reduced purely to an accidental error, which the agreement of the results shows to have been very small (.1 per cent. or less). The preponderant source of error was the difficulty of obtaining uniform temperatures in the electric furnace. A longer and narrower furnace was therefore constructed, in which radiation

TABLE.

Temperature.	Plati	num.	MgCa	Si <sub>2</sub> O <sub>6</sub>	CaSiO <sub>3</sub>		
remperature.	Mean.	Actual.	Mean.	Actual.	Mean.	Actual.	
100°		The state of the s	.1920	.2050	.1833	.1916	
500	.03351	.03560	.2310	.2668	.2170	.2510	
700	.03425	.03685	.2420		.2288		
900	.03515	.03799	.2490	.2810	.2355	.2604	
1100	.03575	.03901	.2563		.2400		
1300	.03644	.04003	.2600	.2800	.2420	.2510	
1500	.03679	.04073					

shields above and below the charge increase the uniformity of temperature. The accidental variations of the results were thus brought in nearly all cases below .5 per cent., usually below .2 per cent. The systematic errors are probably not much larger, but are to be further investigated. Meanwhile, the results seem trustworthy to 1 per cent., except above 1400°, and as little is known of specific heats in the region covered, a preliminary publication of some illustrative substances is now given. The temperature scale was determined from experiments still in progress at the Geophysical Laboratory, and does not contribute appreciably to

Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

the systematic error, except again, possibly, at the highest temperatures. The following values for platinum and two pure crystalline silicates are of the mean specific heat from o up, which was directly determined, and of the actual specific heat at each temperature, derived from this.

The results for CaSiO<sub>3</sub> are within 1 per cent. of those obtained a year ago. These data agree within .5 per cent., in most cases much closer, with the following formulas for the mean specific heat.

Pt .03198+3.4×10<sup>-6</sup># or .03198+3.967×10<sup>-6</sup>#-4.67×10<sup>-10</sup>#<sup>2</sup>, CaMgSi<sub>2</sub>O<sub>6</sub> .1779 + 1.516 × 10<sup>-4</sup># - 1.047 × 10<sup>-1</sup>#<sup>2</sup> + 2.81 × 10<sup>-11</sup>#<sup>3</sup>, CaSiO<sub>3</sub> .1722 + 1.18 × 10<sup>-4</sup># - 6.16 × 10<sup>-8</sup>#<sup>2</sup> + 9.4 × 10<sup>-12</sup>#<sup>3</sup>.

The linear equation for platinum is the more convenient, the other, probably nearer the truth; their difference is well within the possible error.

If  $A + B\theta + C\theta^2 + D\theta^3 + \cdots$  is the expression for the mean specific heat, the actual specific heat is given by  $A + 2B^{ij} + 3C\theta^2 + 4D\theta^3 + \cdots$  but the actual heats thus determined contain the errors of the mathematical expression in an exaggerated degree, hence those here given for the silicates were obtained graphically. Even so, they are less accurate than the mean heats, especially at the higher temperatures (an error of one per cent. in the mean heat at 1500° may produce one of seven per cent. in the true heat). The apparent decrease in the silicate specific heats above 900° must therefore not be given undue weight; but the general character of their specific heat curves, whose increase is mainly at comparatively low temperatures, is unquestionable and in striking contrast to platinum.

Quartz shows the same type, even more strongly marked, but the inversion at 575°, which causes a heat evolution of from 4 to 5 calories, complicates the treatment of the data, and will necessitate further observations. The mean heat, 0-500°, is .2370, which is very much lower than some published values. The specific heats here given for platinum are also several per cent. below accepted values.

GEOPHYSICAL LABORATORY,

CARNEGIE INSTITUTION OF WASHINGTON,
April 6, 1909.

CALORIMETRIC ACCURACY. (METHOD OF MIXTURES.)<sup>1</sup>
BY W. P. WHITE.

I. INCREASE OF THE WORKING TEMPERATURE DIFFERENCE.

THE calorimetric cooling correction is generally computed on the assumption that Newton's law of cooling holds, and to make this assumption tenable, the temperature rise in the calorimeter is restricted

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to a small value, 2 to 4°. A larger interval would diminish the effect of the accidental errors in the thermometer reading, and is easily employed if the law of cooling of the calorimeter is first determined.

In one case, this followed the cubic equation

$$K = .0033^{9} + .000114^{9^{2}} - .0000023^{9^{3}}$$

where  $\vartheta$  is the difference in temperature between calorimeter and jacket. If, now, the difference between this function and the simple function

$$K = .0033\vartheta$$

is tabulated and applied as a correction to the absolute values of  $\vartheta$ , the corrected values of  $\vartheta$  are then proportional to the cooling rate, and may be operated upon precisely as if Newton's law held. The daily variations in the magnitude of the cooling constant are eliminated by this method, iust as by the usual one. The corrections are found graphically and the whole operation hardly requires ten minutes. The possible error from it is far less than several other calorimetric errors. Furthermore the calorimeter temperature usually rises rapidly and then falls slowly, so the final value of 9 when the cooling rate is experimentally determined is near the mean for the preceding interval and the correction on account of the variation from Newton's law of cooling is really very small, - so small that it need only be determined once or twice in the course of a long series of experiments, and may be neglected altogether for work not of the highest accuracy. In a number of different series, with temperature intervals reaching 23°, and a time interval of 14 minutes, its maximum value was .o2 per cent. A great increase in effective thermometric sensitiveness can therefore be obtained with practically no cost, either in labor or chance of error.

### II. Sources of Error.

- r. A bolometer wire .oor mm. in thickness can be heated roo° above the air and will remain not only constant but steady in temperature to .ooor°. There is therefore no reason to suppose that it is at all difficult to so control conditions that the cooling of a calorimeter may be very uniform and dependable, nor is there much, if any, direct evidence to the contrary.
- 2. The necessity of measuring the cooling rate augments, and under favorable conditions about doubles, the error from accidental variations in the thermometer reading. This effect does not depend on the magnitude of the correction, not even when the correction vanishes altogether, unless its being equal to zero can be assured without thermometric measurement.
  - 3. A simple reckoning shows that appreciable error may frequently

arise from neglecting the variation in the temperature of the jacket, but this of course is very easily obviated. The same may also be said of variations of the heat produced by stirring.

Otherwise, the only important source of error due to the cooling arises from its variations before settling down to a steady value, all of which are most conveniently treated as time lags.

- 4. The lag of the thermometer has already been shown to be negligible under ordinary conditions. 1
- 5. If a hot body is in the calorimeter, the temperature of the surface, on which the cooling depends, will for a while lag behind that of the thermometer, by which it is determined.
- 6. On account of the time required to heat the air about the calorimeter, the cooling rate will not at once attain the value appropriate to the measured temperature difference.
- 7. That portion of the cooling which is due to the outlying parts of the calorimeter will obviously lag, since their temperature lags behind the rest.

The error from these lags is easily shown to be insignificant. A calorimeter holding two liters will cool so as to lose about .oo3 of its excess temperature per minute, hence a lag of 20 seconds in the cooling rate means only .1 per cent. final error, nor would this be more than doubled if the calorimeter were reduced to 250 c.c. Now, the lag 5 above need not exceed 2 seconds, hence .o. per cent. is a generous estimate for its effect, and also for the effective value of 7, since that concerns only a small part of the calorimeter surface. Direct measurements show that 6 would rarely reach to seconds. This would, of course, be important in absolute determinations, but in a directly calibrated calorimeter the resulting error is only the variation of the effects with different ranges or methods of heating. But in the case of a single body receiving heat from another, the integral of the lag depends only on the interval and the conductivity, being entirely unaffected by the manner in which the first body is heated, whether slow or sudden, steady or variable, Hence the error from 5, 6 or 7 is confined to the possible slight variations in the integrals of these lags which might result from the fact that they depend upon bodies which are not quite simple - variations which in any case occur only through radical differences in the method of heating, and which affect quantities whose original magnitude corresponds to less than .05 per cent. of the heat measured.

It is clear, then, that under proper conditions, the thermometer reading, rather than the cooling correction itself, is really responsible for the *unavoidable* calorimetric errors. Since in diminishing the size of the calorimeter the need for thermometric sensitiveness decreases at a

<sup>1</sup> PHYS. REV., 27, 526, 1908.

rate approaching the cube of that in which the cooling correction increases, the possible gain from increasing the temperature interval is evident.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
April 6, 1909.

THE RETARDATION OF ALPHA RAYS BY METALS AND GASES.1

By T. S. TAYLOR.

In a paper, in the American Journal of Science, for September, 1908, the writer described some experiments which showed clearly, that the air-equivalents of metal foils decrease with the range of the a-particles entering the foils. By "air equivalent" is meant the amount by which the range of the a-particles in air is cut down by their passage through the foil. The change in the air equivalents is small for thin foils of the lighter metals when the range of the a-particles entering the sheets is high; but when the range is low for thin sheets, or when the sheets are thicker, the change becomes quite marked. By comparing the change for sheets of different metals of nearly equal air equivalents, the rate of change was found to be in the order of the atomic weights of the metals.

Geiger in the Proceedings of the Royal Society  $^2$  pointed out that  $\alpha$ -rays are scattered by their passage through metal foils. This raised the question as to whether the results obtained by the writer were due to the scattering of the rays. This particular point was investigated, and it was found that, although the  $\alpha$ -rays are scattered not only in passing through metal foils but also in passing through the air, the effect previously observed was not influenced by the scattering and hence could not be explained on that basis.

Polonium was used as the source of the  $\alpha$ -rays in the experiments cited above. In order to extend the investigation to  $\alpha$ -particles of greater range, radium bromide has been used as the source of rays in later experiments. The results obtained in this case are in complete agreement with those found in the first experiments. Moreover some other interesting phenomena have been observed. The air equivalent of a sheet of paper does not vary, as it does in the case of the metal foils, with the range of the  $\alpha$ -particle, but remains constant. The same statement holds for a sheet of "celloidin." The air equivalent of a cell containing hydrogen, instead of increasing with the range and consequently with the velocity of the  $\alpha$ -particle, decreases as the range of the entering  $\alpha$ -

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

<sup>&</sup>lt;sup>2</sup> Series A, Vol. 81, No. A 546, p. 174.

particle increases; the thicker the cell of hydrogen, the greater the rate of decrease. The constant values of the air equivalents of the sheets of paper and "celloidin," and the anomalous behavior of the hydrogen sheets may be expected; for the effect we have measured is a relative one, that is, we have substituted the different substances for the air at different points of the range of the  $\alpha$ -particles and made a comparison in this way. Hence, if for those materials having atomic weights greater than that of air, the air equivalents decrease as the range of the entering  $\alpha$ -particle decreases, then for substances such as paper and celloidin having atomic weights about the same as air, we should expect their air equivalents to remain constant; but, on the contrary, for a lighter substance, such as hydrogen, we should expect its air equivalent to increase as the range of the  $\alpha$ -particle decreases.

Using the same source of rays, the Bragg ionization curves have been obtained in an atmosphere of hydrogen, and in an atmosphere of air reduced in pressure so as to have the range in air the same as it was in hydrogen. The curves obtained in the two cases present differences which are in accordance with the phenomena cited above.

SLOANE LABORATORY, YALE UNIVERSITY, March 31, 1909.

# REDETERMINATION OF THE RADIATION CONSTANTS OF A BLACK BODY.<sup>1</sup>

BY W. W. COBLENTZ.

THE radiation from the so-called black body was investigated about eight to ten years ago and the results then obtained are somewhat at variance. In view of the fact that it seems feasible to replace or at least to supplement the present thermoelectric extrapolations, at high temperatures, by means of a temperature scale based upon these radiation laws, it is desirable to make a thorough spectrobolometric investigation of the black body at various temperatures.

In previous investigations it was thought that an accuracy of about three per cent. had been attained. In order to attain a still greater accuracy very elaborate provision must be made in everything that pertains to the work.

In the present investigation an electrically heated radiator is being employed. The temperature within the radiating cavity is uniform to within 0°.5 for a distance of 6 to 8 cm. from the central radiating wall (or over a total length of 12 to 16 cm.). During any series of observa-

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

tions the temperature is maintained constant to 0°.2 to 0°.3 — no observations being made when a greater variation occurs.

The bolometer of platinum, .0004 mm. in thickness, 4.2 ohms, is placed in the focus of a hemispherical mirror. Its rear side is left bright and its front side is painted with a thin coating of a mixture of lamp black and platinum black, in alcohol. A bit of camphor is added which prevents the mixture from "creeping" while drying, and ultimately evaporates. When dry the front side of the bolometer is smoked a little. This would seem to render the bolometer about as "black" as one can expect to make it. The resistance of the bolometer for various battery currents as well as its temperature coefficient are known.

Contrary to some of the prevailing notions, the uncertainties in the measurements are located in the bolometric end of the apparatus instead of in the constancy of the temperature of the radiator.

Two series of spectral energy curves at various temperatures from 500° to 1490° C. have been obtained — in all 33 different curves. The observations extend over a long period in which there were days when the sensibility of the apparatus, the temperature of the room, or the humidity, etc., varied, so that some of the errors due to these causes ought to be minimized in the final results.

The data are not sufficiently worked out to make a more definite statement than that after a three-hour run it has been possible to repeat the observations in different parts of the spectrum with an accuracy of 0.1 to 0.5 per cent., and that the  $\lambda_{\max}T$ -constant seems to be as high as any value heretofore obtained.

THE PLATINUM THERMOMETER AT HIGH TEMPERATURES.1

By C. W. WAIDNER AND G. K. BURGESS.

THIS is an experimental investigation of the applicability of the Callendar formula for the calibration of platinum thermometers, in the range oo to 1100° C., for platinum of different degrees of purity.

Platinum temperatures are numerically defined in terms of the resistance of platinum as follows:

$$pt = \text{IOO}(R - R_0)/(R_{100} - R_0)$$

and the difference between platinum and gas scale temperatures is given by the formula:

 $t - pt = \delta(t/100 - 1)t/100.$ 

The fundamental interval F.I. is evidently  $R_{100} - R_0$ , and the funda-

<sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

<sup>2</sup> To be published shortly in the Bulletin of the Bureau of Standards.

mental coefficient,  $c=(R_{100}-R_0)/100R_0$ . The constants  $\delta$  and c are characteristic of the material of the thermometer. Calibrations are made at 0°, 100°, and 444°.70°C. (the boiling point of sulphur) giving the values of  $R_0$ ,  $R_{100}$ , and  $R_s$ , respectively, from which data any other temperature may be computed from the observed resistance, R.

Nine platinum thermometers were used of wire varying in diameter from 0.1 to 0.6 mm. and having a range of  $R_0$  from 0.11 to 21.3, of c from 0.0039 to 0.0017, and of  $\delta$  from 1.50 to 1.80. The thermometers were of the compensated and of the potential lead types; some of the measurements were taken by a potentiometer method, some by means of a special Wheatstone bridge, and some of the thermometers were adapted to measurements by three methods, the potentiometer, the Wheatstone bridge, and the Kelvin double bridge.

The resistance measurements were made to 1 or 2 parts in 100,000.

The metals were used in crucibles of pure graphite with powdered graphite covering them and in amounts of 1.5 to 2 kilograms, ensuring ample depth of immersion of the coil of the thermometer. The melting and freezing point determinations were carried out in vertical electric resistance furnaces wound with two platinum ribbon heating coils on concentric porcelain tubes, the windings being so spaced as to give quite uniform temperature distribution throughout a considerable length of the furnaces. The temperature could be maintained constant to within a few hundredths of a degree for many minutes at a time, during the freezing or melting of the metal. By stirring with the thermometer, undercooling could be practically avoided.

The results of the freezing-point determinations are shown in the table. It will be seen that for pure platinum, for which  $\delta = 1.50$ , the Callendar equation is in agreement with the generally accepted gas scale to within the limits of reproducibility of the latter, or  $1^{\circ}$  C., but for impure platinum this equation no longer holds.

The effect of high temperatures on the constants of platinum thermometers is, in general, to reduce the value of  $R_0$  and increase F.I. The effect on  $\delta$  is very small. Measurements made with pure platinum thermometers of heavy wire (diameter = 0.6 mm.) without the usual mica supporting frame, show unusually small changes in  $R_0$  even after several heatings for some hours each at 1250°, changes equivalent to only a few tenths degree C.

Thermometers of pure palladium were also tried, for which  $\delta = 2.89$  and c = 0.00336. They do not satisfy the Callendar equation; for example, it leads to a value of 1152°C. for the F.P. of copper. The effects due to heating are similar to those found for platinum.

Four Pt, Pt-Rh thermocouples, of slightly differing composition, calibrated in terms of the equation  $T = a + bE - cE^2$  at three of the

Scale of Platinum Thermometer. Callendar Formula. Calibration Data: Ice Steam, Sulphur ( $S = 444^{\circ}.70 \text{ C.}$ ).

-	$\delta = 1.505$ . $c = 0.00385$ to 390.					$\delta = 1.570$ . $c = 0.00206$ to 210.					$\delta = 1.803.$ $c = 0.00173.$			born
ai.	calc.	ن <u>ا</u>	Number of		ပ	ů.	N	Number of		ŭ	· .	Obs,	Ho Day.	
Metal.	Temp, ca	Range deg.	Obs.	Samples.	Ther- moms.	Temp, calc.	Range deg.	Obs.	Samples.	Ther- moms.	Temp. calc.	Range deg.	No. of Ob	Sca
Sn	5 231.92	0.04	4	1 K	2		0	1						
- 1	231.89	.09	6	3	2	231.8		4	3	1				
Cd	321.01	.09	3	K	2	320.9	.02	2	1	1				321.7
Pb	327.58	.01	2	1	1	-				-				326.9
	( '	) .04	6	K	1	(	∫ .08	8	3 K	1		1 - 3		
Zn	419.37	11. 5	9	3	1	419.3	2 7 .16	11	- 5	1				419.0
Zn	1	δ =	_ 1.	516		1	( 8:	<u>`</u> 1.	551	*	* 0			
	419.30	( .06	5	K	1	419.2	8 {	1	K	1		-	. 1	
Sb	630.71	.57	7	3 K	2	631.2	5 .17	4	3 K	1	632.65	0.09	2	630.6
M.P.	630.80	.15	4	2 K	1	631.0	.08	3	3 K	1				
Ag-Cu	779.55	.08	3	1	2	781.2	1 .06	2	1	1				
71-29											J - 2			
Ag-Cu	779.18	.45	6	1	3								7.0	
72-28			-											
Ag-Cu	779.23	.30	3	1	2		ŀ				784.61	.14	2	
73-27	1		1	1:-			1			1		1,000	10	1. 4. 5
Ag	960.88	.39	8	1	3	966.2	1 .02	2	1	1	975.28	.08	2	961.5
Cu	1083.04	1.61	7	B.C.	Ŵ.3	1091.9	2 1.15			1	1106.2	1 3 7	1	1084.1
	1082.88	2.26	13	4	4			1		-			7	

<sup>&</sup>quot;Range" = difference between highest and lowest F.P. determinations.

freezing points in the table (Zn, Sb, Cu or Zn, Ag-Cu, Cu), as given by the platinum resistance thermometer, agree with each other to within o°.3 at intermediate temperatures, and to within 1° with the scale as defined by the thermometer of pure platinum.

Note on Radiation Due to Impact of  $\beta$ -Particles Upon Solid Matter.<sup>1</sup>

By C. DAVISSON.

A nattempt has been made to detect the existence of a non-deviable type of radiation similar to X-rays, due to the impact of  $\beta$ -particles upon solid matter, or, at least, to reduce the limits of experimental error within which it may be said such radiation is not to be observed.

<sup>&</sup>quot;Number of samples" refers to materials from different chemical firms.

<sup>&</sup>quot;K"="Kahlbaum," "B. C. W."= Baltimore Copper Works' purest product.

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

The method of procedure has been to concentrate the  $\beta$ -radiation from five milligrams of radium bromide along the axis of a strong magnetic field; to interrupt this concentrated radiation by means of a metallic target and examine the radiation proceeding from the target at right angles to the direction of the field. A field of from 3,500 to 4,000 lines per cm. has been found sufficient to concentrate the greater part of the  $\beta$ -radiation into two streams of a centimeter or less in diameter, proceeding in opposite direction from the radium along the lines of force. The individual  $\beta$ -particles move in spiral orbits but in the aggregate they form a cylindrical stream analogous to the cathode stream. On intercepting one of these streams by means of a lead target inclined to make the angle of incidence about 45 degrees, it has been found that the ionization inside a closed vessel whose center is 45 cm. from the target, on a line through its center at right angles to the direction of the magnetic field, is increased by about twenty ions per c.c. per sec.

It should be stated that the intensity of the magnetic field between the target and the closed vessel is not uniform but decreases almost uniformly from the target outward at the rate of 9 per cent. of its maximum value per cm. to a point where its value becomes negligible.

Various shadow-casting experiments which have been carried out to date do not indicate conclusively that the radiation reaching the ionization chamber from the target is propagated in straight lines. They receive ready explanation, however, on the view that the radiation is, in fact, rectilinear but that it appears to be otherwise on account of a deviable tertiary radiation from solid bodies in the neighborhood of the beam examined. Modifications are being made in the apparatus at present by means of which it is hoped a definite answer may be made to this question.

Shielding experiments have indicated that the radiation is quite soft, its effect being halved when o.r mm. of lead foil is interposed between the target and the ionization chamber.

Experiments with targets of different material have indicated that the radiation from them is an increasing function of their atomic weights.

A more detailed account of these and other experiments bearing on the same subject is in preparation.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
April 14, 1909.

PRELIMINARY NOTE ON THE VARIATION WITH SPEED OF THE

Mass of an Electron.

By C. A. Proctor.

THE general arrangement of apparatus was similar to that employed by S. Simon for the determination of e/m, with the addition of a <sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

condenser in the discharge tube to admit of measuring the electric deviation of the rays. The electric deflection was computed from the magnetic by the Lorentz and Abraham formulæ and the result compared with the observed deflection.

A large number of observations at velocities varying from 0.13 to 0.44 the velocity of light give a mean deviation of computed from observed deflections of +0.45 per cent. in the case of the Abraham formula, and of +1.05 per cent. in the case of the Lorentz-Einstein formula.

## THE NATURAL SCALE OF PURE COLOR.1

By P. G. NUTTING.

STEINDLER has made determinations of the least difference in wavelength that are perceptible as differences in color. Reciprocals of these values give the relative sensibility of the eye to wave-length differences throughout the spectrum. But sensibility is the derivative of scale reading, hence integration of the sensibility curve gives color as a function of wave-length. The visible spectrum was divided into 25 parts representing 25 steps of equal color difference on the theoretical scale and comparison with a suitable normal spectrum showed no perceptible errors.

# An Experimental Determination of the Resolving Power Constant of Lenses.<sup>1</sup>

By P. G. NUTTING.

WITH a half-tone screen of about 200 lines to the inch illuminated with monochromatic light as object, the resolving power of a F/3 to F/20 lens may be determined with considerable precision. Theory gives

$$\varphi = a \, \frac{\lambda}{h}$$

as the least angular separation between two objects just resolvable by a lens of diameter 2h used in light of wave-length  $\lambda$ . Viewing two stars, the image of either is calculated to lie at the center of the first dark diffraction ring surrounding the other when a = 0.61.

With the half-tone screen the following determinations of a were made:

All structure leaves image when	a = 0.48
Nature of object apparent when	a = 0.54
Image shows proper form but lacks contrast when	a = 0.65
Shadows just perceptibly hazy when	a = 0.05

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

Hence the theoretical value of a assumes an image agreeing in form with the object but greatly lacking in contrast and without clear shadows.

THE EFFECT OF TEMPERATURE UPON THE ABSORPTION SPECTRA OF VARIOUS SALTS IN SOLUTION.<sup>1</sup>

By W. W. STRONG.

THE present work is a continuation of that reported upon by Jones and Strong <sup>2</sup> and is being carried on by a grant from the Carnegie Institution of Washington.

The apparatus is the same as previously described with the addition of prisms and a temperature bath by means of which the temperature of the solution could be changed. The length of solution in the path of light could be varied between 3 and 250 mm. The method is due to Dr. Anderson and works very well for solutions that do not evaporate rapidly.

Salts of chromium, cobalt, uranium, nickel and copper have been investigated between 0° and 90° C. in water over a region of the spectrum between  $\lambda$  2100 to  $\lambda$  7600. Wratten and Wainwright red sensitive films are used. Erbium, neodymium, præsodymium and potassium salts are being worked at present. Later these salts will be worked in different solvents up to the critical temperature of the solvent.

All the salts investigated show increased absorption as the temperature rises. The absorption bands widen in every case as the temperature is increased. At the same time several of the uranyl bands appear to shift towards the longer wave-lengths without changing very greatly in intensity. This may be due to dehydration of the uranyl group. Many of the wider bands broaden unsymmetrically, the broadening on the red side usually being the greater.

Note on the Rate of Movement, Depth and Intensity of Storms.<sup>1</sup>

By WM. R. BLAIR.

- 1. The vertical distribution of moisture in the atmosphere.
- 2. The change in temperature with altitude and its relation to the moisture distribution.
- 3. The variation with altitude of the velocity of the prevailing westerly winds upon which storm movement seems to depend.
- 4. The influence of these three factors on storm intensity and the conclusion that, for a given location and season, deeper storms move faster

Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

<sup>&</sup>lt;sup>2</sup> Phys. Rev., Feb., 1909, pp. 143, 144.

and bring about the more abrupt also the greater changes in weather conditions.

TEMPERATURE CHANGE WITH ALTITUDE IN THE LOWER STRATUM
OF THE ATMOSPHERE AND ITS RELATION TO SURFACE
AIR PRESSURE AND OTHER PHENOMENA.

By WM. R. BLAIR.

- 1. Diurnal variation of temperature.
- 2. The aperiodic variation depending on the succession of cyclonic and anticyclonic conditions.
- 3. Characteristic changes in the temperature during the passage of an area of high pressure. During the passage of an area of low pressure.
  - 4. The relation of the gradient to the vertical air movement.

# The Determination of the Constants of Instrument Transformers.<sup>1</sup>

By P. G. AGNEW AND T. T. FITCH.

THE constants to be determined are the ratios and phase angles between primary and secondary. In the case of potential transformers this is accomplished by drawing from the source of supply, a small current through a high non-inductive resistance, and applying the secondary to this resistance potentiometer fashion, using as a detector the moving coil of a dynamometer whose field coil is in the primary circuit. This makes the ratio depend directly on two bridge values of resistance. The phase angle is obtained with the same set-up by applying the small resultant e.m.f. to the moving coil of a dynamometer whose field is excited by a current in quadrature. A maximum sensibility of 1/20,000 in ratio and of o. 1' of phase angle is obtained. A similar method is used for the ratio and phase angle of current transformers. Measurements on a considerable number of transformers showed that the potential transformer is an instrument of high precision, and that the same is true of the current transformer but to a less degree. It was found that in case the secondary of a current transformer be open circuited while current was passing through the primary, the constants were changed, due to the permeability of the iron being decreased, but that this effect could be removed by demagnetization.

In connection with the work a method was developed for the comparison of extremely low inductances, 10<sup>-7</sup> henry, or lower, with an accuracy of one per cent.<sup>2</sup>

<sup>&</sup>lt;sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 26 and 27, 1909.

<sup>&</sup>lt;sup>2</sup> This paper will appear in full in the Bulletin of the Bureau of Standards.

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